Development of High Performance Concrete Using Combinations of Mineral Admixtures

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ABSTRACT

Cement replacement materials are by-products used to produce high performance concrete.

Published data on the effects of combinations of mineral admixtures in concrete on the microstructural and performance-related properties under different curing regimes are comparatively little. Further the correlation of strength of concrete to its permeability and pore structure is also not clear.

The main objective of this research is to study the performance of various combinations of fly ash/silica fume and slag/silica fume concretes under three different curing regimes, viz. continuous moist curing, no moist curing after demolding and air drying after 7-days of initial moist curing. Six different concrete mixes were prepared with ordinary portland cement and a blend of portland cement and combinations of fly ash+silica fume and slag+silica fume .The water-to-cementitious materials ratio of all the concrete mixtures was kept constant at 0.45.

The properties investigated included ①workability of the fresh concrete, ②engineering properties such as cube and modified cube compressive strength, flexural strength, dynamic modulus of elasticity, pulse velocity, shrinkage and swelling, ③permeability and ④ microstructural properties such as porosity and pore size distribution.

The results show that prolonged dry curing results in lower strengths, higher porosity, coarser pore structure and more permeable concretes. It was found that the loss in early age compressive strength due to incorporation of fly ash or slag can be compensated for by the addition of small amounts of silica fume. The engineering and microstructural properties and permeability of concretes containing fly ash or slag appear to be more sensitive to poor curing than the control concrete , with the sensitivity increasing with increasing amounts of fly ash or slag in the mixtures. The incorporation of high volumes of slag in the concrete mixtures refined the pore structure and produced concretes with very low porosity and threshold diameters. The results emphasize that a minimum 7-day wet curing is needed for concrete with mineral admixtures to develop the full potential, and that continued exposure to a drying environment can have adverse effects on the long-term durability of inadequately cured slag or fly ash concretes. The results also confirm that compressive strength alone is not an adequate index to judge the performance of concrete, and the knowledge of the strength, pore structure and permeability are required for this purpose. Slag/silica fume concrete mixtures showed

better performance than fly ash/silica fume concrete mixtures as regards the development of engineering and microstructural properties.

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ABBREVIATIONS and NOTATIONS

OPC	Ordinary Portland Cement
SF	Silica Fume
FA	Fly Ash
slag	Ground granulated blast furnace slag
Control	Mix comprise only OPC , kg/m^3
FA/SF	Mix comprise combination of OPC+SF+FA ,kg/m^3
slag/SF	Mix comprise combination of OPC+SF+slag ,kg/m^3
W	Control 350 OPC mix kg/m^3
X	300 OPC+ 20 SF+30 FA mix , kg/m^3
Y	250 OPC+ 20 SF+80 FA mix , kg/m^3
Z	250 OPC+ 20 SF+80 slag mix , kg/m^3
ZX	300 OPC+ 20 SF+125 slag mix , kg/m^3
ZY	250 OPC+ 20 SF+165 slag mix , kg/m^3
wet-cured	Continuos moist curing
7d wet/air-cured	7 day continuos moist curing and then exposed to lab environment
air-cure	No curing after demoulding
R.H.	Relative Humidity
w/c	Water/Cement ratio *
f_{cu}	Compressive strength , Mpa
f_f	Flexural strength, Mpa
E_d	Dynamic modulus of elasticity ,Gpa
k	Intrinsic permeability , m^2
MIP	Mercury Intrution Porosimitry

* w/c ratio for mixes refers to water/cement+SF+FA or water/cement+SF+slag

CHAPTER ONE

INTRODUCTION

1.1 Introduction

Concrete in its various forms is probably the most widely used construction material in the world. It is essentially a mixture of fine and coarse aggregate bound together by a hardened cement paste. The use of concrete as a construction material is not a recent development, but dates back to ancient times, several thousand years ago. The ease with which concrete can be made allows anybody to mix and fabricate it, since the concrete mix will harden to a great degree even if it is not made with the right proportions or not placed properly. However, the durability of that concrete is not expected to be similar to that of properly constituted, placed or cured concrete which exhibits a long service life under most natural and industrial environments.

1.2 Durability and its significance

The durability of concrete is one of its most important properties and a long service life is considered synonymous with durability. Since durability under one set of conditions does not necessarily mean durability under another, it is customary to include a general reference to the environment when defining durability. For example, existing specifications have led to a deterioration of numerous structures in the Arabian Gulf area. Until very recently, these specifications were very simple in that they prescribed the compressive strength and minimum cement content, and also the cover of the reinforcement, which are insufficient to prevent deterioration of concrete. The situation soon changed, and the nature of the specification, the mix proportions and the conditions of exposure, linked to each other, were considered. According to ACI [1] committ 201, and other researchers, durability of portland cement concrete is defined as its ability to resist weathering action, chemical attack, abrasion or any other process of deterioration, that is, durable concrete should be capable of withstanding the conditions for which it has been designed throughout the life of a structure. Cabrera [2] stated that durability is not an intrinsic property of a material, but rather a function which relates the performance of the material to its service life under various environmental conditions.

No construction material is inherently durable; as a result of environmental interactions, the microstructural properties of concrete changes with time. A concrete is assumed to reach the end of its service life when its properties, under a given set of conditions of use, have deteriorated to such an extent that with continuing use it becomes unsafe or uneconomical. Lack of durability can be caused by external agents arising from the environment or by internal agents within the concrete. Causes responsible for concrete deterioration can be physical or chemical or a combination of both. With chemical processes, sulphates, acids, seawater, and chlorides can be transported from the environment into concrete and induce corrosion of steel reinforcement. In fact water tends to be central to most durability problems in concrete, and is known to be the cause of many types of physical and chemical degradations. Only temperature conditioned crack formations and mechanical wear can take place without water.

Perhaps the most important consequence of the nature and manufacturing process of concrete in the field is to know that it is a characteristically porous material and will always remain so; microcracks and micropores will always exist on the surface of concrete, providing a path for transport of aggressive elements into the interior of concrete [3]. Permeability and pore structure are, therefore, of critical interest and could be the most important parameters influencing the durability of concrete. However, whatever improvements are made in the formulation of the concrete material and the control of its quality, they are not likely to produce a totally impermeable concrete that will completely prevent the ingress of potentially harmful events throughout its life.

1.3 Concrete in the Arabian Gulf

Although many concrete structures have shown excellent durabilty for over 50 years, there is now a world-wide problem of deterioration caused primarily by reinforcement corrosion which is recognised as the most critical factor affecting the durability of concrete structures. Expensive diagnostic survey and repair programmes are now common.

The severity of the environment of the Arabian Gulf region, for concrete construction has been widely recognized as a consequence of the evidence of widespread premature degradation and deterioration of concrete structures. In the Arabian Gulf countries, the corrosion of reinforcing steel and the resulting concrete deterioration appears to be more severe than that in other parts of the world. Reinforced concrete structures, only 10 to 15 years old, have shown significant deterioration due to reinforcing steel corrosion [46]. The surroundings of concrete structures in the Arabian Gulf area are highly contaminated with chloride, sulphate and carbonate salts. Reinforcing bars can corrode before being placed in concrete (rust formation) or inside concrete. Corrosion of reinforcing steel with the resulting spalling and cracking of concrete is the predominant cause of failures in the Gulf area, although other forms of concrete deterioration, including sulphate attack, salt weathering and non-structural cracking due to shrinkage and thermal gradients also cause deterioration [7].

The prevailing hot and humid climate, the aggressive environment of coastal regions, the lack of good quality raw materials free of contamination in some regions and the relative scarcity of skilled force in conjunction with the lack of strict compliance with specifications have collectively created adversaries to concrete construction [8]. In spite of these facts an actual common code of practice has still not been established for the Middle East region although good and serious progress has been made.

Many concrete structures in Bahrain are suffering from symptoms of deterioration within a short span of 10 to 15 years. The low durability performance of concrete due to insufficient care taken during the design and construction combined with harsh environment have led to this premature deterioration which could be averted. For example, the 64 pile caps on the two bridges which comprise the Manama-Sitra causeway have been found to be at risk from corrosion due to the ingress of chloride ions from the aggressive marine environment of Bahrain; these pile caps were constructed in 1975. Also, numerous highway bridges, built several years ago as part of the development of modern highway networks in the Gulf States, have suffered prematurely from excessive cracking and loss of serviceability. These deteriorations emphasize the urgent need for an enhanced durability-based criteria for the design and execution of concrete structures in this region.

The deterioration process itself of concrete is not the result of one factor, one process or one set of aggressive agents. Various durability studies and surveys of deterioration in structures have identified the cause of such degradation in a hostile environment. However, it is interesting to know that two of the most significant deterioration mechanisms in the Gulf aggressive environment are:

- Reinforcement corrosion, and
- Chemical attacks

Corrosion destroys primarily the reinforcement and chemical attacks destroy primarily the concrete. The presence of water and salt are believed to be the most decisive in these mechanisms.

The Concrete Society [9] in its technical reports discussed the three principle factors which cause deterioration of reinforcement, viz:

a: low cover to steel
b: permeable concrete
c: high chloride levels

Swamy [10] stated that the three major factors that encourage the transport mechanism of aggressive agents into concrete and influence significantly its service behaviour, design life and safety are cracking, depth and quality of cover to steel and the overall quality of the structural concrete. These three factors have an interactive and interdependent, almost synergistic, effect on the control of intrusion into concrete of external aggressive agents such as water, air, chloride and sulphate ions.

1.4 High performance concrete

Generally it is accepted that a durable concrete which possess high strength and low permeability and porosity is one of the best means to ensure the integrity of concrete subjected to environmental attack. The use of cement replacement materials has become an essential component of a global strategy required in the development of high performance concrete [11,12]; their economic and engineering benefits have already been well established. To provide the desired corrosion protection to steel, the concrete develops its characteristics, quality or durability, primarily on the basis of its cement component. Portland cement is now more likely to be blended with mineral admixtures such as fly ash (FA) slag and silica fume (SF), alone or in combination, in order to enhance the basic characteristics of the resulting concrete, both in its fresh and hardened states.

In recent years blended cement concrete, because of its long term performance, has received considerable acceptance in the marine environment of the Arabian Gulf where a growing volume of investment in concrete construction is located. In addition to off-shore oil industry structures, a causeway between Saudi Arabia and Bahrain has recently been constructed at a cost of £410 million. A new Manama-Muhara bridge and UmmNassan island Jett, costing hundreds of millions of pounds, are under construction now in Bahrain, and with these formidable financial outlays, there remains deep concern that these concrete structures will be durable and free from excessive maintenance and repairs. The blended ordinary Portland cement (OPC)-slag or OPC-SF cement has been especially recommended for use in the construction of these structures.

From the above discussion it can be seen that any attempt to alleviate the deterioration risk therefore implies producing concrete capable of withstanding attack by aggressive agents. The incorporation of FA/SF and slag/SF in this project aims at activating this by improving the mechanical properties, pore structure, and permeability of concrete through enhanced mix design and good curing. The research attempted is to show a way forward by which it is possible to exploit and derive the hidden advantages of combinations of FA/SF and slag/SF to produce a stronger and more durable concrete for the aggressive environment. This study investigates, beside the control mix, two types of FA/SF and slag/SF mixes differing in cement replacement levels, with 350 and 450 kg/m^3 total cementitious content which are usually used in construction. The durability aspects of these concrete systems under various curing conditions were investigated. The project is divided into three parts: (1) mechanical properties of the mixes, (2) pore structure, and (3) permeability of the different cured mixes. The experimental programme of this study comprises casting a large number of concrete prisms placed in three curing regimes to reflect practices on site. In other words the work strategy reported in this thesis is to cover:

(i) weather environment (external factors)
(ii) concrete materials and properties (internal factors)

1.5 Aims and objectives

Most researchers studying the effect of fly ash, silica fume and slag on the durability of concrete, have concentrated their effort on the idea of adding only one blending agent with cement to the concrete specimens, and curing them well, either by covering with plastic bags to prevent any loss of moisture of the specimens, or by immersion in water before conducting any durability tests.

However, from a review of current literature, it was felt that the amount of published data on the effect of combinations of fly ash or slag and silica fume mineral admixtures on the engineering and microstructural properties of concrete is rather limited. Also in spite of the great impact of moisture on the properties of concrete and its performance, very little, work has been carried out on the performance of concrete mixtures with combinations of fly ash/silica fume and slag/silica fume under curing regimes which are likely to represent the behaviour of concrete in real conditions.

Therefore, information on the performance of concrete without and with a combination of cement replacement materials needs to be obtained under various curing conditions, which represent the curing to which concrete would be subjected in practice; such performance includes the durability of concrete in addition to strength, dynamic modulus, pulse velocity, shrinkage, as well as pore structure and permeability.

This study, therefore, is aimed to obtain a high performance durable concrete with a practicable range of combinations of fly ash and silica fume, and slag and silica fume that would yield concrete with satisfactory high strength, exceeding 50 MPa and good microstructure using the maximum amount of fly ash and slag and minimum amount of silica fume (i.e. maximum economy).

The main objectives of the study are:

1. To develop a durable concrete mix with good workability and high-early-strength to withstand harsh environmental conditions.

2. To study the mechanical properties of these concrete mixes in terms of changes in strength and elasticity properties with time: a) compressive and flexural strength, b) dynamic modulus of elasticity, c) pulse velocity, and d) shrinkage and swelling.

3. To establish the effects of curing regime with age on the above mechanical properties.

4. To assess the effect of concrete containing a combination of different mineral admixtures cured under different curing regimes on the oxygen permeability of concrete mix.

5. To study the porosity and pore size distribution of OPC concrete and concretes with combinations of cement replacement materials. Various blended agents will be studied.

1.6 Thesis layout

This thesis consists of seven chapters. In Chapter 1, a background of the research related to the durability and deterioration of concrete in an aggressive environment such as the Gulf area is briefly discussed. The aims and objectives of the research are then defined.

In Chapter 2, the literature related to cement replacement materials used in concrete mixes and their effects on engineering and microstructural properties are reviewed.

In Chapter 3, details of the experimental programme carried out in this research are described. It comprises the properties of ordinary portland cement, fly ash, slag, silica fume, superplasticizers and fine and coarse aggregates. It also includes the grading curves of both fine and coarse aggregates. Methods of mixing, casting and curing are presented as well as details of concrete mixes and tests carried out.

In Chapter 4, the engineering properties such as workability, compressive and flextural strength, dynamic modulus of elasticity, pulse velocity, and shrinkage and swelling of different concrete mixes as affected by curing regimes and cement replacement materials are presented and discussed. The relationship between compressive strength and both flexural strength and dynamic modulus is also established.

In the first part of Chapter 5, details of mixes and procedure of sampling and testing for porosity and pore size distribution by using the mercury intrusion porosimetry technique are presented. It also includes pore size distribution determination, which involves the theory, contact angle, effect of sample drying, apparatus and presentation of results. In the second part of this chapter, results obtained on porosity and pore size distribution obtained by mercury intrusion porosimetry are analysed and presented. The results are also discussed and compared as affected by different curing conditions and cement replacement materials.

The results of oxygen permeability are presented and discussed in Chapter 6. The test was carried out by a new gas permeameter designed by Cabrera and Lynsdale [13]. Results include the influence of curing regimes as well as the influence of age of curing. Three curing regimes were investigated and three ages for testing were considered (7, 120 and 240 days). The effect of replacing cement with FA/SF and slag/SF was also investigated. Details of the experimental method used for permeability testing are also given, including the theory, apparatus and preparation of specimens.

In Chapter 7, the overall conclusions drawn from Chapters 4, 5 and 6 are summarized, and recommendations for future research are presented.

Finally, the references used in the introduction of this thesis and those used in the literature review, experimental programme and discussions are listed.

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

Literature relating to blended cements in concrete and the effect of curing regimes on this concrete are numerous. In this chapter, only literature concerning those aspects related to this particular research i.e. the mechanical and microstructural properties of hardened concrete incorporating FA, SF and slag as a mineral admixtures added to concrete made with the portland cement are discussed. This survey also includes the effect of curing conditions on the various properties of concrete.

2.2 Curing and its significance

The supposed benefits of curing are widely accepted but in practice, curing is often ignored or ineffective. Regardless of the cement or the blends of cementitious materials used, concrete must be kept in a proper moisture and temperature condition, during its early stages if it is to fully develop its strength and durability potential. The investigation carried out in this study is attempting to show that curing is really necessary for the development of desired properties. The necessity of curing arises from the fact that hydration of cement and the pozzolanic reaction can take place satisfactorily if the concrete is kept moist. The potentially harmful effects of loss of water by evaporation shall be prevented either by applying water of preventing excessive evaporation. Various materials, methods and procedures for curing concrete are available but the principles involved are the same; to ensure the maintenance of a satisfactory moisture content and temperature so that durability properties may develop. Figure 2.1 illustrates the frequency with which the various techniques are recommended [14,15]. The method of application and duration of curing varies depending on the type of concrete and on the conditions where concrete will be placed and cured. From site practice the wet hession curing method for a minimum period of 7 days being the most popular. The CIRIA Report [14] reported that 22% of the publications dealing with concrete curing recommended this period and that the wet hessian curing method was the most frequent one.

Among the advantages to be gained from effectively applied curing, those of early strength and microstructure development and reduction in shrinkage are perhaps the most well-established, these properties can be examined on test specimens. However,

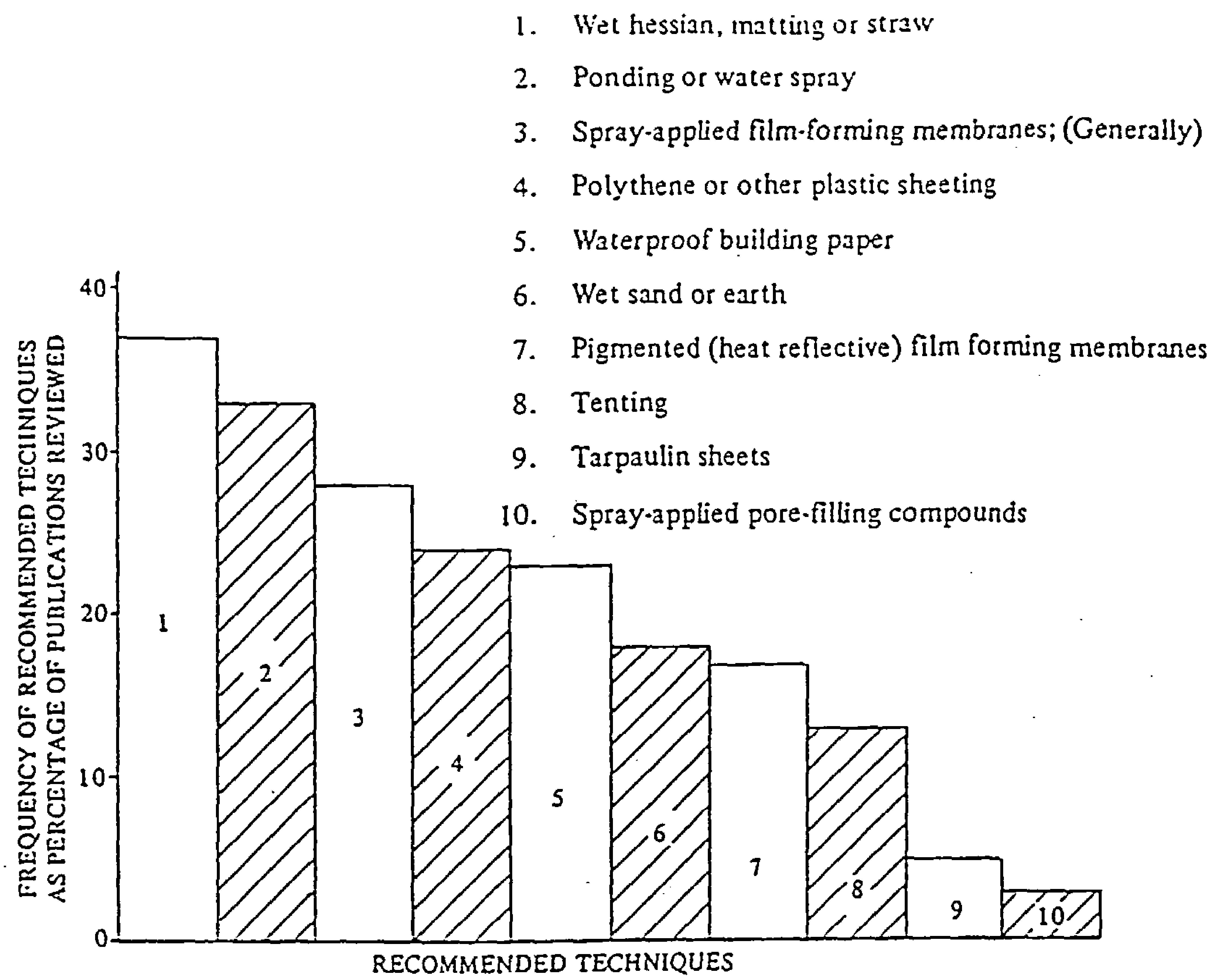
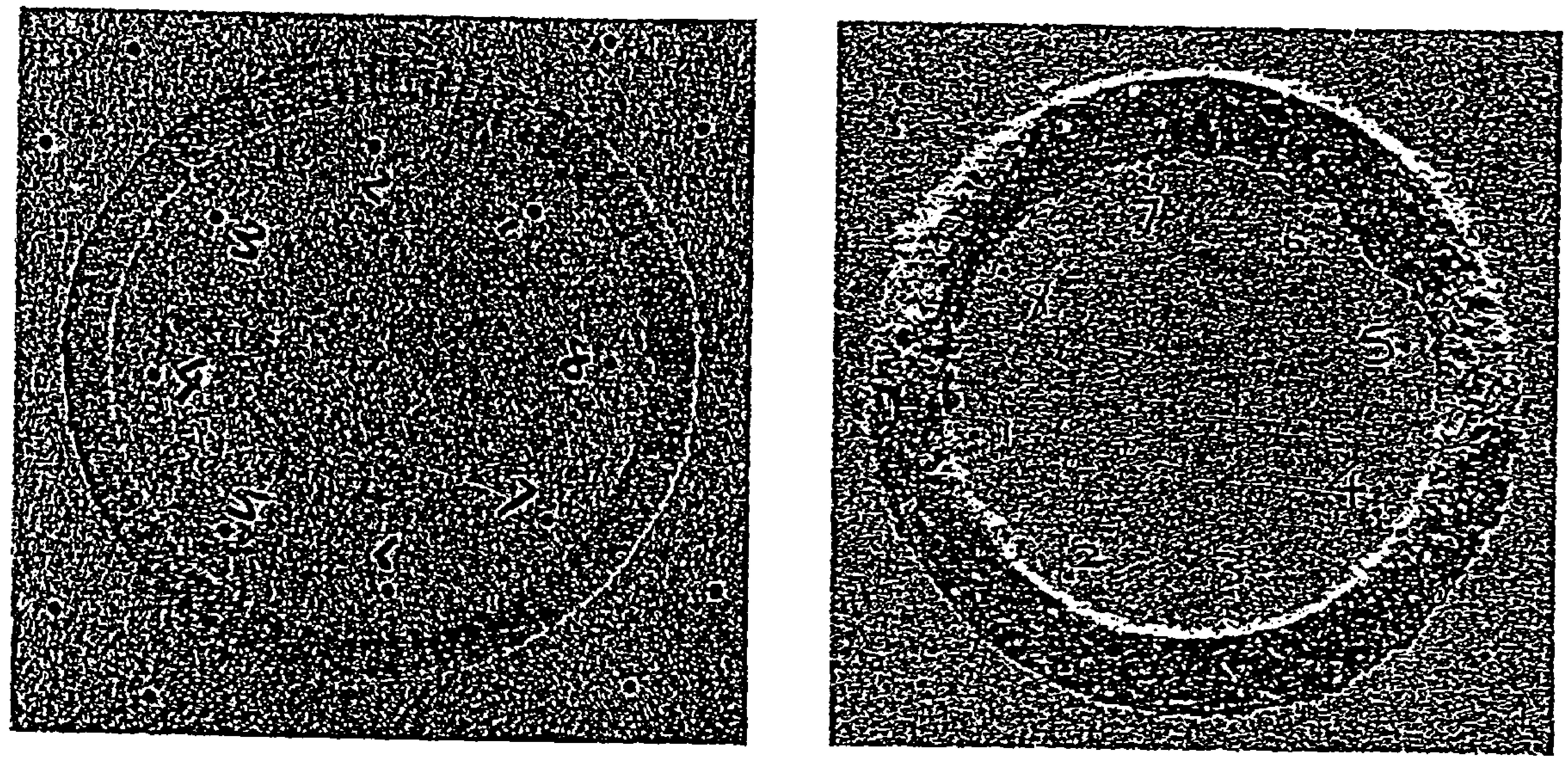


Figure 2.1 Curing techniqes [14].


(a) Cured for 7 days under polythene sheeting

(b) Slab not cured

Figure 2.2 Drying effect on a slab containing 50% slag cement [18].

with cement replacement materials such as FA, SF and slag curing takes on a much more important role than with portland cement concrete [14,11]. FA/SF and slag/SF concretes can therefore be expected to need longer curing periods where strength and durability are recognised as a potential problem. In practice, the effects of curing cannot be divorced from the development of engineering properties of concrete [16]. For example, BS 8110 [17] requires longer curing periods for FA and slag concretes than for OPC concretes, and, given the slower rate of strength gain. However, the equivalent 28 day strength concretes containing slag are more vulnerable to poor curing than either plain OPC or OPC/FA concretes [18].

Swamy [16,19] showed that slag concretes with 50 and 60% cement replacement need longer wet curing than OPC concrete, and that on the other hand in situations where no water curing occurs, slag concretes with 50% cement replacement continued to hydrate, whereas OPC concrete virtually stopped all hydration after 28 days. Similarly it is suggested that somewhat longer periods of moist curing for the FA concrete is needed [11]. The above discussion does not mean that, in order to produce a durable concrete, those made from portland cements need no curing whereas those made with slag or FA cements do. There is no doubt that as with all cementitious materials, the rate and degree of hydration is affected by the loss of moisture at an early age, with a decrease in strength gain. To attain proper strength and durability adequate curing is essential regardless of the type of cement, but more care is needed when FA,slag and SF are used.

Results of this study have indicated that wet curing improved the potential strength of microstructure concrete. Price [20] showed that in a reinforced concrete building, not moist-cured and where the members receive no moisture after construction, the concrete in the structure may never reach the strength level of the 28-day moist-cured specimens.

Long and Kurtz [21] described the effects of various curing methods on the durability of laboratory specimens as measured by changes in the modulus of elasticity. Such effects on companion three-and-a-half-year-old trials walls in the field were 'slight'.

The results obtained by curing concrete pavements and other exposed forms of flat-slab construction are well known, the most familiar being a marked reduction in the incidence of shrinkage cracks which may eventually involve expensive repair work and traffic disruption [14].

Many references to curing in the CIRIA report [14] concluded that properties such as strength, pore structure, permeability, resistance to weathering, abrasion, and cracking may well be improved by the thorough application of proper curing, and that absence of adequate curing in tropical and arid countries can have very damaging effects.

The adverse effect of a drying environment on strength, dynamic modulus pulse velocity, pore structure and permeability is shown in this study. Swamy [16] reported that when exposed to drying slag concretes with high levels of cement replacement, 50 and 65%, showed some retrogression of strength and elastic modulus with aging, internal microcracking was also detected by pulse velocity measurements due to prolonged drying. The shorter the curing and the greater the degree of drying, the worse is its effect upon durability properties [22].

Floors and screeds are particularly sensitive to poor curing, as abrasion resistance depends upon the top few millimetres of concrete [18], Figure 2.2 shows an example of drying effect on a slab containing 50% slag cement. Mangat and El-Khatib [23] showed that dry curing at early ages results in higher intruded pore volume, coarser pore structure and higher absorption of the surface zone compared with initial moist curing for 22% FA , 9% SF and 40% slag mixes of 0.45 water/binder ratio. Patel et al [24] reported that drying of concrete at an early age leads to restricted hydration in the surface layer and thus to higher porosity and permeability. Graf and Grube [25] also reported that initially air-cured OPC and FA concretes result in a higher coefficient of permeability than concretes which were provided with an initial curing which did not allow evaporation of water to take place.

However, it should be remembered that most of the technical benefits associated with the case of cement replacement materials in concrete (viz. high strength and durability) cannot be achieved until the pozzolanic reaction has progressed; for this, a minimum wet-curing (presence of moisture) is essential. Therefore, after casting the concrete, concrete containing FA, SF and slag must be protected from drying especially on site. In hot/dry weather, in addition to customary precautions against moisture evaporation, effective measures should be taken for maintaining the concrete temperature until sufficient cement hydration has occurred to ensure a continuation of the cementitious/pozzolanic reaction.

2.2.1 Hot-weather curing

Hot weather introduces many problems in manufacturing, placing, and curing concrete that can adversely affect the properties and serviceability of the hardened concrete. Curing is very important due to both higher concrete temperatures and increased rates of evaporation from the fresh mix. For example in Bahrain, concrete plants add ice blocks to the ready mixed concrete during transport up to the point of delivery to the construction.

The durability, strength, and other characteristics of concrete in hot climates are critically dependent on its treatment from the moment it is compacted and during the first few weeks afterwards, and inadequate curing can negate all the earlier care taken in mix design and concreting operations, and can also lead to serious defects such as plastic shrinkage cracking and excessive drying shrinkage [15].

Table 2.1 [26] summarizes the principle factors of importance and likely effects on concrete in the Middle East arid or extremely arid climates where excessive loss of water by evaporation leads to reduced amounts of water retained below that necessary for development of engineering properties. Figure 2.3 [27] shows the effect of air temperature, concrete temperature, relative humidity and wind velocity, on surface evaporation rate. Because of these climatic conditions (higher temperature and greater the sunshine) the general awareness of the importance of curing in production of durable concrete is nowadays taken into account. In Bahrain, on the all government construction projects curing of in-situ concrete is a must. Concrete should be cured in hot weather in accordance to ACI Committee 305 report, and water curing, if used should be continuous to avoid volume changes due to alternate wetting and drying [28]. The committee states that the need for adequate continuous curing is greatest during the first few days after placement of concrete in hot weather.

Shalon and Ravina [29] describe the effect of curing conditions and time of pouring concrete in hot countries and find, in particular, that continuous water curing is more effective than the use of sealing compounds. Proudley [30] states that curing is an important factor with report to ultimate strength and durability and that 'optimum' curing is essential to obtaining the maximum potential quality of concrete. His report concluded that curing procedures are dependent on variables such as humidity and ambient temperature, and that the intended use of a structure may raise the question of the degree of curing which is most economical for the situation.

Neville [31] describes the influence of curing on concrete strength, and discusses the process of cement hydration in relation to moisture evaporation and its dependency on temperature, relative humidity and wind velocity. He said that evaporation rates, could be described in terms of 'drying tendency'. In fact concrete curing requirements in any geographical situation are influenced by the climatic conditions, relative humidity and

Table 2.1 Climatic factors of importance and likely effect on concrete [26].

Typical Climate	Effect on Concrete
high ratio of evaporation to precipitation very high temperature - up to 50°C with up to 20°C variation in a day at the coast - somewhat greater inland rapidly fluctuating humidity up to 70% variation in one day, which can be typically as high as 90°C on the coast and as low as 10°C inland minimum cloud cover leading to intense solar radiation drying winds	plastic settlement cracks; plastic shrinkage cracks; drying shrinkage cracks; surface crazing; big and rapid slump loss and hence high water/cement ratios; concrete lacking in durability due to high temperature during hydration; thermal cracking.

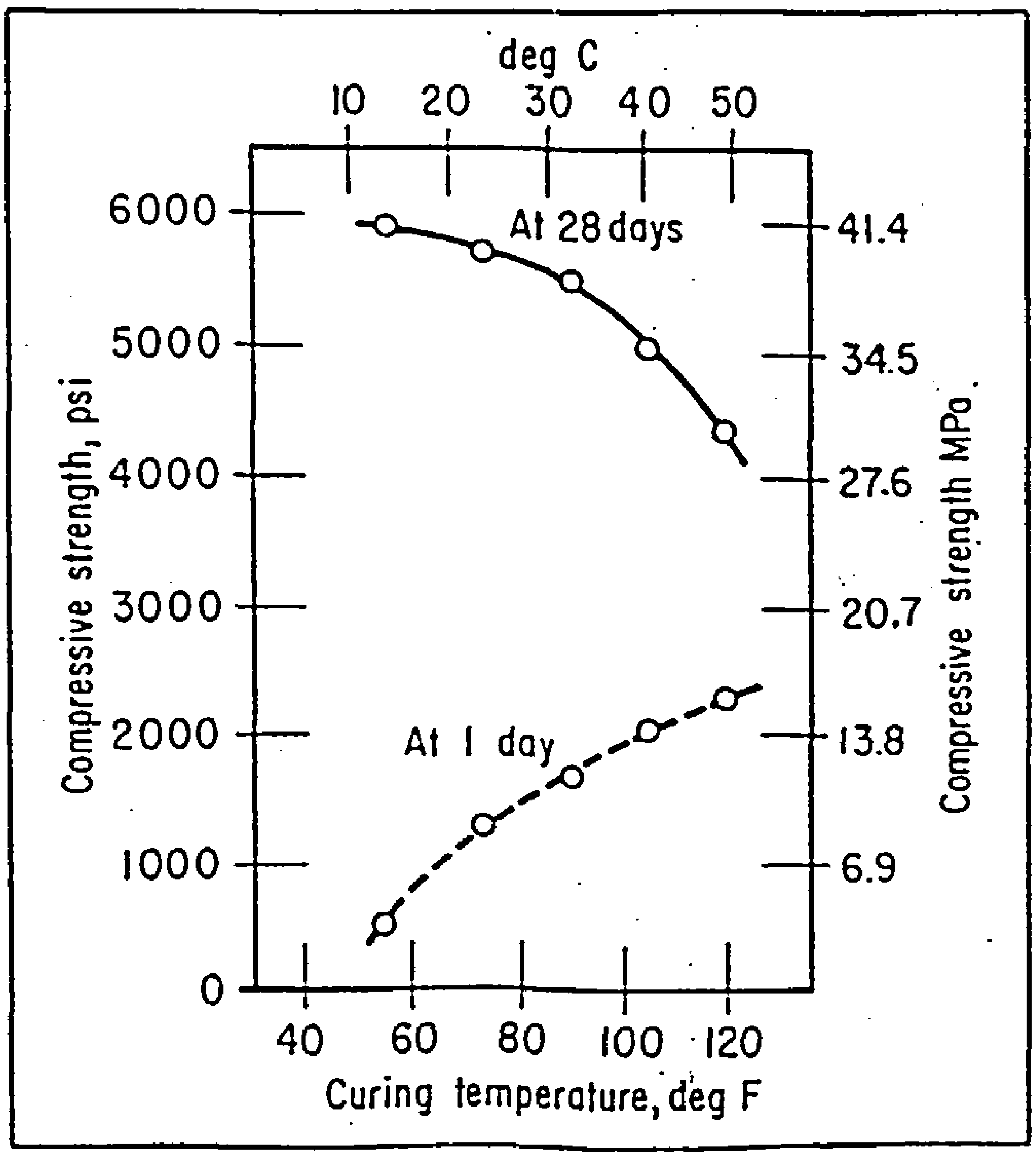


Figure 2.3 One day strength increase with increasing curing temperature but 28-day strength decrease with increasing curing temperature[27].

temperature particularly in hot countries. Mills [32] found that even if efficient curing membranes are used, hydration ceases very quickly if concrete is exposed to a dry atmosphere, because of the effects of self-desiccation.

However, it can be concluded that a country which experiences a hot climate is more demanding in its curing requirements that one which has a temperate climate, and the concrete surface should be either watered or protected from evaporation. Also, since the benefits obtained from applied curing are vital to ultimate performance of the concrete, the costs should be involved.

2.3 Concrete with mineral admixtures and its properties

There are strong economic, technical and ecological arguments for the use of siliceous admixtures as a port replacement of cement, and thus as a desirable and vital constituent of concrete [33]. Many of these siliceous admixtures are industrial by-products such as FA, slag and SF. Good quality concrete can be obtained by relatively high cement content in the mix, low water/cement ratio, and strong well-graded aggregates. This is true if adequate curing is provided. Durability of concrete is deemed to be improved by replacing some of the cement with cement replacement materials such as FA, SF and slag.

Work on durability of concrete involves various aspects. Perhaps the most important of all are the strength, pore structure and permeability. The lower the strength and the larger the open pore volume, the more likelihood for an aggressive agent to penetrate into the concrete and thus corrosion initiation. Strength and microstructural properties give an indication of the performance of concrete, and their development is intimately associated with the curing regime. In fact curing regimes play an important role in determining the pore structure and permeability of blended cement concrete and hence affects its durability.

2.3.1 Workability

The workability and pumpability of concrete mixture is enhanced by decreasing the friction between aggregate particles, and this is generally achieved by increasing the paste content of the mixture [34].

The relative densities of OPC, FA and slag are approximately 3.1, 2.3 and 2.9. thus, a kilogramme of FA will occupy 35% more solid volume than a kilogramme of OPC, whilst a kilogramme of slag will occupy 7% more solid volume. For equal weight of cement and equal mix water contents, this increase in the powder volume seems generally of benefit to the workability in mixes with low cement contents or where fine aggregate lacks some of the finer fraction [18].

Replacement of OPC by FA in concrete often improves workability, the water reduction associated with fine mineral powders is not a mechanical effect, but the result of dispersion and deflocculation similar to the effect of organic admixtures [16]. The most significant benefit of FA complying with BS 3892: Part 1 is the reduction in water content which can be achieved with a given concrete workability [35].

Replacing of OPC by slag on an equal weight to weight basis in a concrete generally leads to a small increase in powder volume in the mix, which may be one reason why there is only a small increase in the workability [11,18]. Another reason for improvement in workability could be due to slag that has a surface texture that is much smoother than that of cement [11]. In reality, however, the influence of slag on the workability of concrete is not clear, especially when measuring workability by standard methods such as the slump test [11].

In this study the use of slag, at about 30% and 40%, plus SF (6 to 8%) leads to a general improvement in workability and reduced the dosage of superplasticiser to half.

On the other hand, if SF is used with FA or slag in concrete, water demand is expected to increase due to the very fine vitreous particles of SF which have a very high surface area compared to OPC, FA and slag. The major effect of SF on the workability of concrete are to increase the cohesiveness and stability of the mix (consequently, bleeding is reduced). The increased cohesiveness means slump loss. Sellevold [36] reported that in concrete with a cement content of more than 250kg/m^3, the water demand will increase when adding SF or even replacing cement on a 1:1 basis, when no water-reducing agents are used. Carette and Malhotra [37] also measured water demand in SF concrete, and concluded that water demand increased with an increasing SF amount and that water-reducing agents should be dosed. The slump loss due to incorporation of SF could be compensated by the use of water-reducing agents.

In fact with blended cements, the use of a superplasticiser is an essential for mix proportioning. It maximises the full-strength-producing potential of SF in concrete and assists greatly in reducing mixing time [38]. Superplastisisers are also integral to the requirements of both early-age and long-term strength development, they initiate sufficient cement hydration at a very early stage to activate pozzolanic action and keeps up both reactions at a continuing rate [39]. Also, from the standpoint of evaluation of the effect of SF incorporation, the strength comparisons between concrete mixtures both with and without SF are meaningful only if the water/binder ratio is held constant by the use of superplasticisers in concrete containing the SF which is generally the practice when more than 5% SF by weight of cement is used [11]. For practical purposes it is generally recommended that the slump should be 20-30 mm higher for SF concrete to obtain the same workability as that for normal concrete [36].

Specific examples of how FA, SF and slag generally effect slump, workability, bleeding and other characteristics of fresh concrete are found in the book edited by Swamy [11] and three reports published by the ACI [38,40,41].

2.3.2 Early-age and long term strength development

The early and long-term strength development of any portland cement depends upon the continuing presence of moisture for hydration. In situations where hydration can continue, there is evidence [11,18] that OPC/FA and OPC/slag concrete gains proportionately more in strength (long-term) than does an equivalent OPC concrete. Continuing hydration in the longer term is advantageous in that the resulting improvement in concrete properties helps to resist physical and chemical degradation of the concrete.

Mix design is also very important to the rate of strength gain which depends upon it. Usually concrete is produced to comply with specification, and either 28 day strength of cement content or water/binder ratio can be the controlling criterion in the mix design. If the w/b ratio is controlling the concrete mix, i.e. fixed, a water reducer is likely to be used. In this study the w/b ratio was kept constant (0.45) and superplasticiser was used to maintain a slump of 100 to 150 mm.

A large number of research reports have been published dealing with the effect of cement replacement materials on the strength of concrete. These were concerned primarily with the use of either FA or slag or SF as a partial replacement for a addition to portland cement.

Both the ultimate strength and the rate of strength gain depend on the amount and characteristics of the mineral admixture (viz., particle size distribution or surface area, and the amount of reactivity of glassy phrase), the composition of the concrete mixture (viz., cement content and type, water/cement ratio, and the presence of other admixtures), and curing conditions (viz., concrete temperature and environment humidity) [34].

In fact both the strength development rate and the ultimate strength are controlled by the hydration and pozzolanic reactions of cement and mineral admixtures, because strength development is related to pore-fill process which takes place with the formation of hydration products.

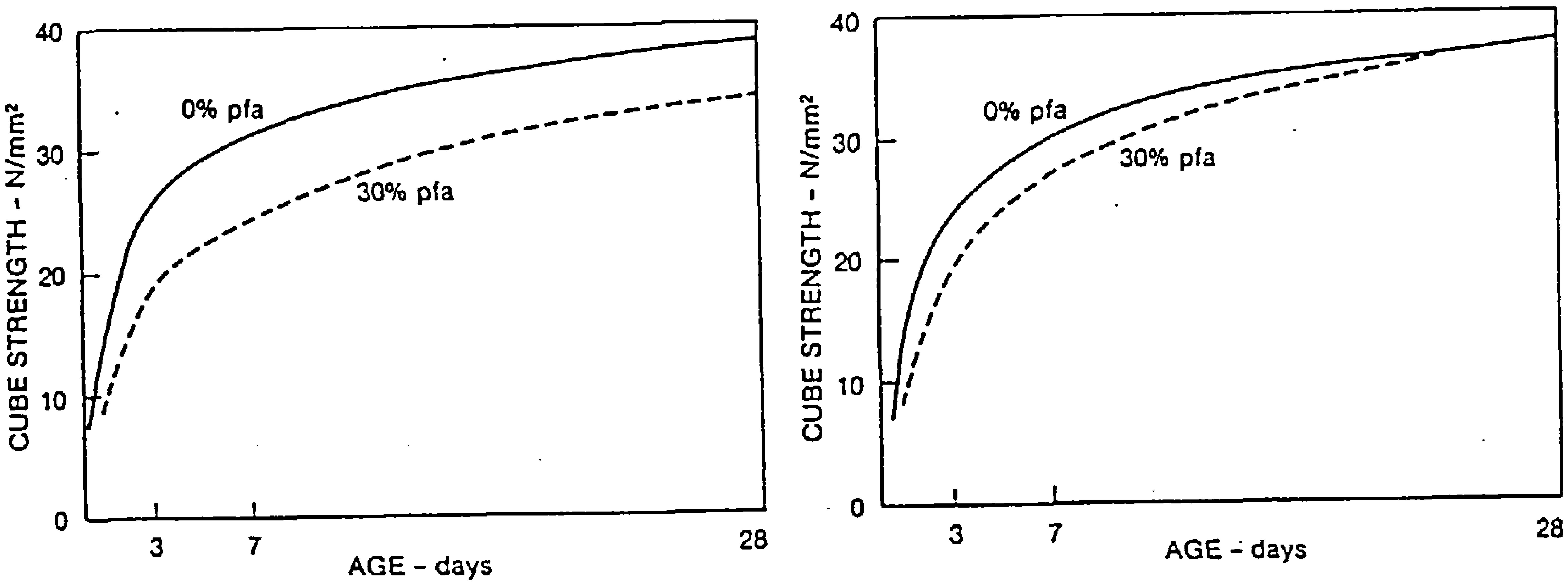
It is well known that early-age strength of concrete incorporating slag or FA is generally lower than the strength of concrete incorporating 100 percent portland cement, even though the later-age strength development of such concrete is equal to or higher than the control concrete [42].

In fact the beneficial effects of the use of slag and FA can not be reflected on early-age strength because of the hydration reactions in the case of slag concrete, and the pozzolanic reactions in the case of FA concrete proceed at relatively slow rate.

Figure 2.4 shows the pattern of strength development for slag concretes for mix designs which have equal cement content and workability or equal 28 day strength and workability [18]. For mixes designed on the basis of equal 28 day strength and workability using 40% slag, the 3 day strength is about 50-60% that of the OPC concrete and at 7 days about 65-75%. Similarly, using 70% slag, these figures drop to about 30-35% at 3 days and 50-65% at 7 days [18]. However, these data are indicative of the trends and do not necessarily represent the lower and higher ranges of the strength development. In both cases the strengths are lower than OPC mixes.

Similarly, concretes made with FA and with equal cement contents and workability have lower early ages strengths and lower 28 day strengths. Figure 2.5 [18] shows that 25% FA mix gave 7 day strengths about 75% of the OPC control and 28 day strengths about 80 to 90% of the control. The strength at 3 and 7 days of FA concretes of equal 28 day strength is about 90% of the OPC concrete [18].

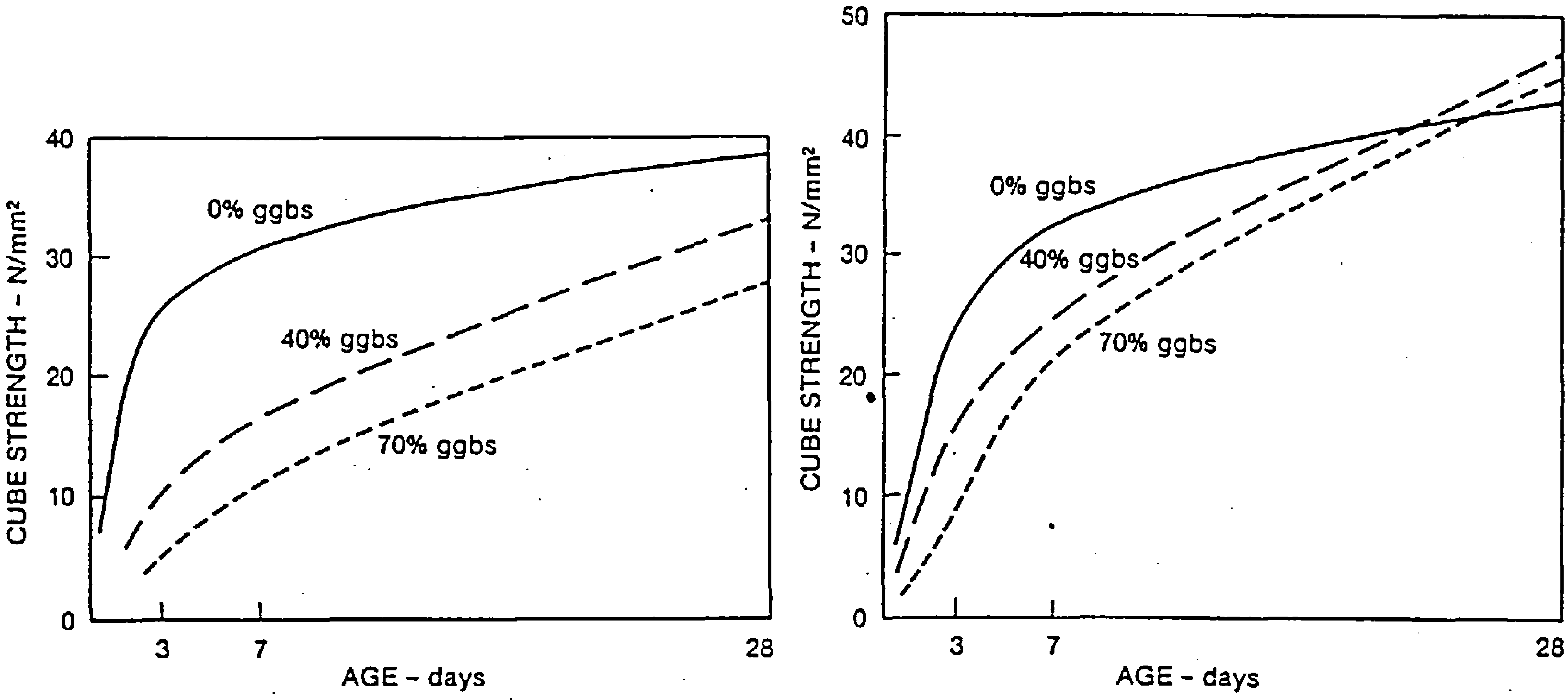
Ramezanianpour and Malhotra [43] reported an investigation in which the performance of slag, FA and SF concretes were studied under four different curing regimes. The water-to-cementitious materials ratio of all the concrete mixtures was kept constant at 0.50, except for the high-volume FA concrete mixture, for which the ratio was 0.35. The concrete specimens were subjected to moist curing at room temperature after



(a) Equal binder content and workability

(b) Equal 28 day strength and workability

Figure 2.4 Early strength gain of slag concretes at 20 C [18].



(a) Equal binder content and workability

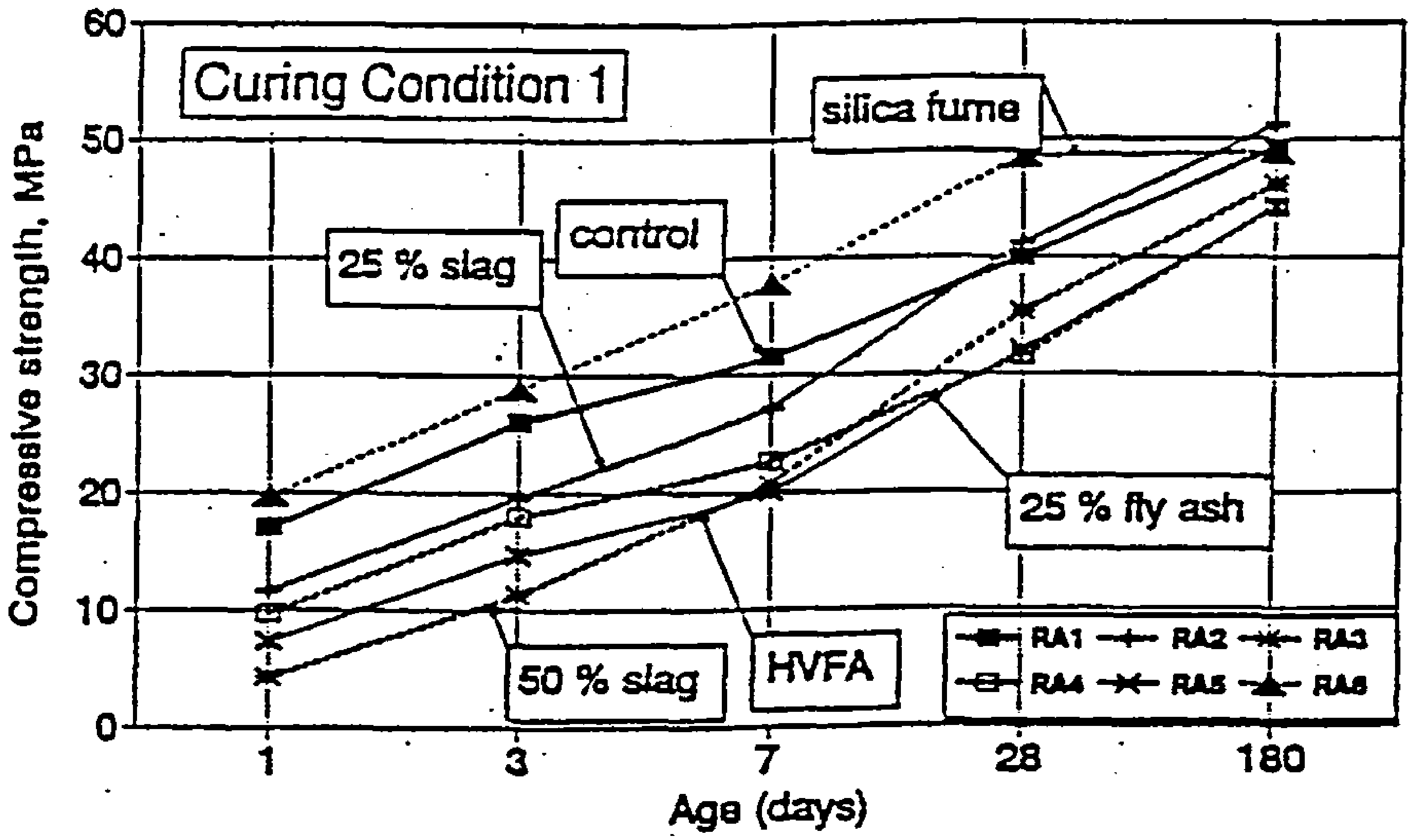
(c) Equal binder content and workability

Figure 2.5 Early strength gain of fly ash concretes at 20 C [18].

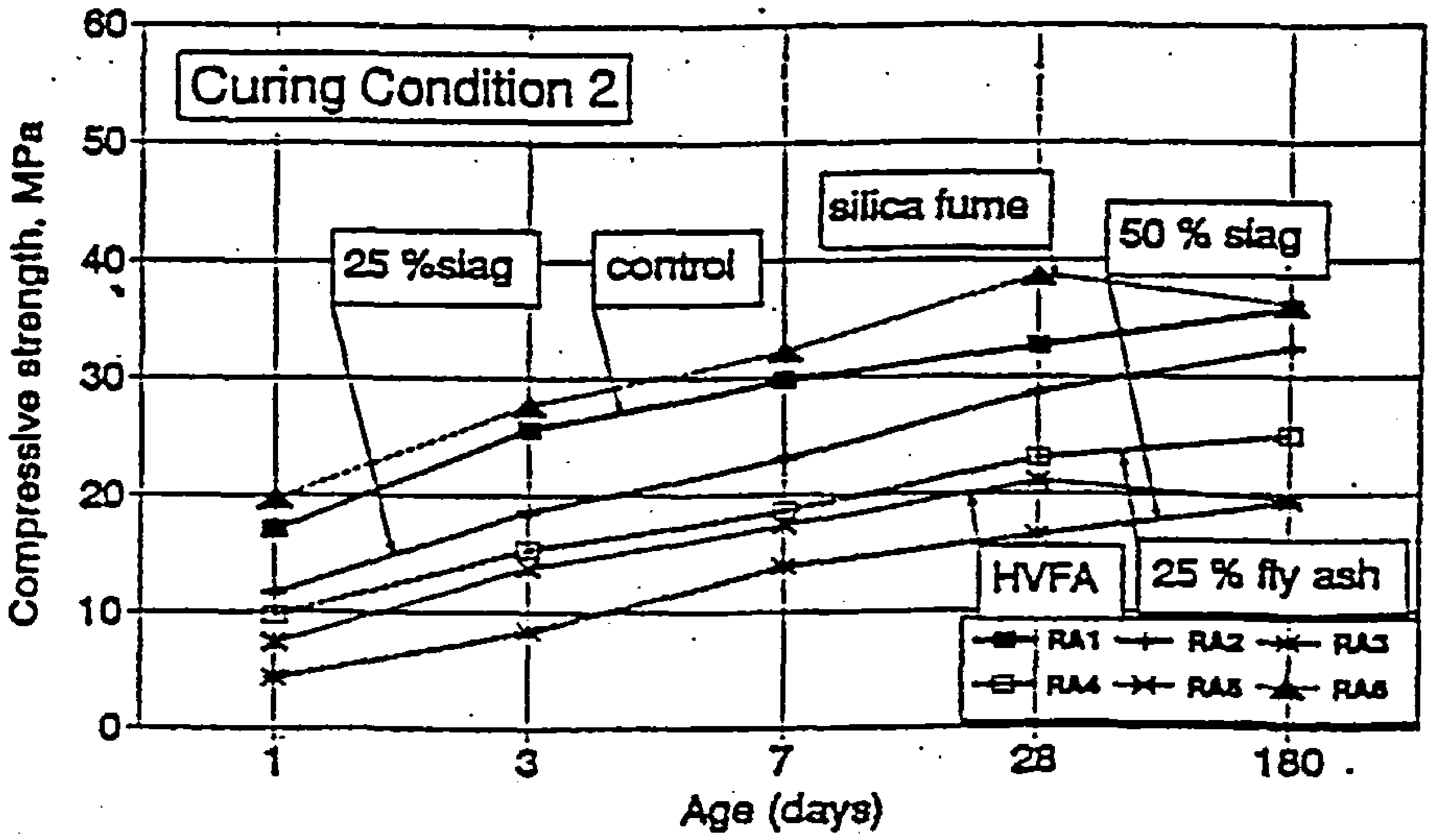
demoulding, curing at room temperature after two days of moist curing, and curing at 38°C and 65% relative humidity. Their compressive strength results at various ages are shown in Figure 2.6. It can be seen that highest strength is obtained for concrete incorporating 10% SF, followed by control concrete, concrete incorporating 25% slag, concrete made with 25% FA and the concrete with 50% slag (the lowest), respectively. At 28 days, SF concrete still had the highest strength with a value of 48.4 MPa. This was followed by 25% slag concrete, control concrete, 50% slag concrete and 25% FA concrete, respectively. They [43] found that the lowest compressive strength value at 28 days was 31.5 MPa for 25% FA concrete. Between 28 and 180 days, SF concrete showed almost no strength gain whereas all other concretes showed a continuous gain in strength and reached strength values between 44.3 and 51.1 MPa, the highest value being for concrete with 25% slag. They concluded that the high-strength gain for the slag and FA concrete are due to the inherent cementitious properties of the slag and pozzolanic reactivity of FA.

Swamy and Boukini [19] reported an investigation to obtain a 50 MPa 28-day strength concrete having 50 and 65% by weight cement replacement with slag having relatively low specific surface. The 1-day strength of slag concrete was consistently low compared to OPC concrete, about 50% of the corresponding OPC concrete strength at 50% replacement level, and about 30% at 65% replacement level. However, with their [19] adopted mix proportioning method, strength of both slag concretes at 3 and 7 days was highly comparable to that of the corresponding OPC concrete, and reached nearly the same values as the control OPC concrete. The compressive strength values at 7 days were 38.5, 38.5 and 36.8 MPa for OPC control, 50 and 65% slag concretes, respectively.

From the above discussion, it is seen that the early strength development for FA and slag concretes are lower than OPC concretes, and that rate of early strength gain can only be described in relative terms. This low early strength results due to that FA and slag, with their much coarser particle size distribution and low specific surface (typically 300 to 500 m^2 kg) make little strength contribution at very early ages (up to 3 days), some contribution during the intermediate period (3 to 14 days), and considerable contribution thereafter [34]. With finer particle size and increasing calcium content, slags and high-calcium fly ashes usually tend to accelerate the rate of strength gain [34]. On the other hand SF with very high content of non-crystalline silica and high surface areas (20,000 to 60,000 m^2/g) are able to make some contribution to the strength of a given concrete mixture even at very early ages of hydration (viz., 1 to 3-d), significant contribution during the first 2-4 weeks, and relatively little contribution thereafter [34].



a- Compressive strength development of wet-cured concrete .



b- Compressive strengh development of dry-cured concrete at room temperature .

Figure 2.6 Compressive strength of slag,fly ash and silica fume blended cement concretes vs age [43].

Typical strength development characteristics of SF concrete are shown in Figure 2.7 and 2.8 [38]. Figure 2.7 gives data for concrete with SF as a direct replacement by mass for portland cement, and Figure 2.8 refers to concrete with SF as an admixture portland cement-FA concrete. The one-day compressive strength of SF concrete is generally equal to or higher than the strength of control concrete regardless of whether the SF is used as a direct replacement or as an admixture. However, at 28 days the compressive strength of SF concrete is always higher and in some instances markedly so, as shown in Figure 2.7 and 2.8.

Therefore, it was considered that the problem of low early age strength could be solved by using a mixture of high reactive pozzolans such as SF and normal pozzolans such as FA or slag.

Carette and Malhotra [44] have reported a results of laboratory investigation to determine the early-age strength development of concrete containing 30% of FA as a partial replacement for cement and incorporating various percentages of SF ranging from 5 to 20%, when the w/c ratio of 0.4 was kept constant in all concrete mixtures by the use of a plasticiser.

Malhotra and Carette [42] reported results of an investigation on the early and later-age strength development of concrete incorporating 50% pelletized blast furnace slag, to which small amounts of SF have been added. The amount of SF ranged from 0 to 20% by combined weight of portland cement plus blast furnace slag.

They [42,44] concluded that the use of SF in concrete incorporating 30% FA and 50% slag as a partial replacement of portland cement resolved the problem of low early-strength, and at or beyond age of 7 days for FA and 14 days for slag the loss in compressive and flexural strengths of concrete due to incorporation of FA or slag can be fully compensated for by the given addition of SF. Their compressive strength versus age results are shown in Figure 2.9.

Mehta and Gjorv [45] have reported a data using this approach, in his investigation 30% portland cement in concrete was replaced by an equal volume of FA, SF, or a 50:50 mixture of the two. He found that the 7 days strength was similar to that of control concrete and the 28-days and 90-days strengths were respectively, 42 and 51% higher. He concluded that from the standpoint of early concrete strengths, it is better to use mixtures of low and high surface-area pozzolans, such as fly ash and condensed silica-fume, than using a normal pozzolan alone.

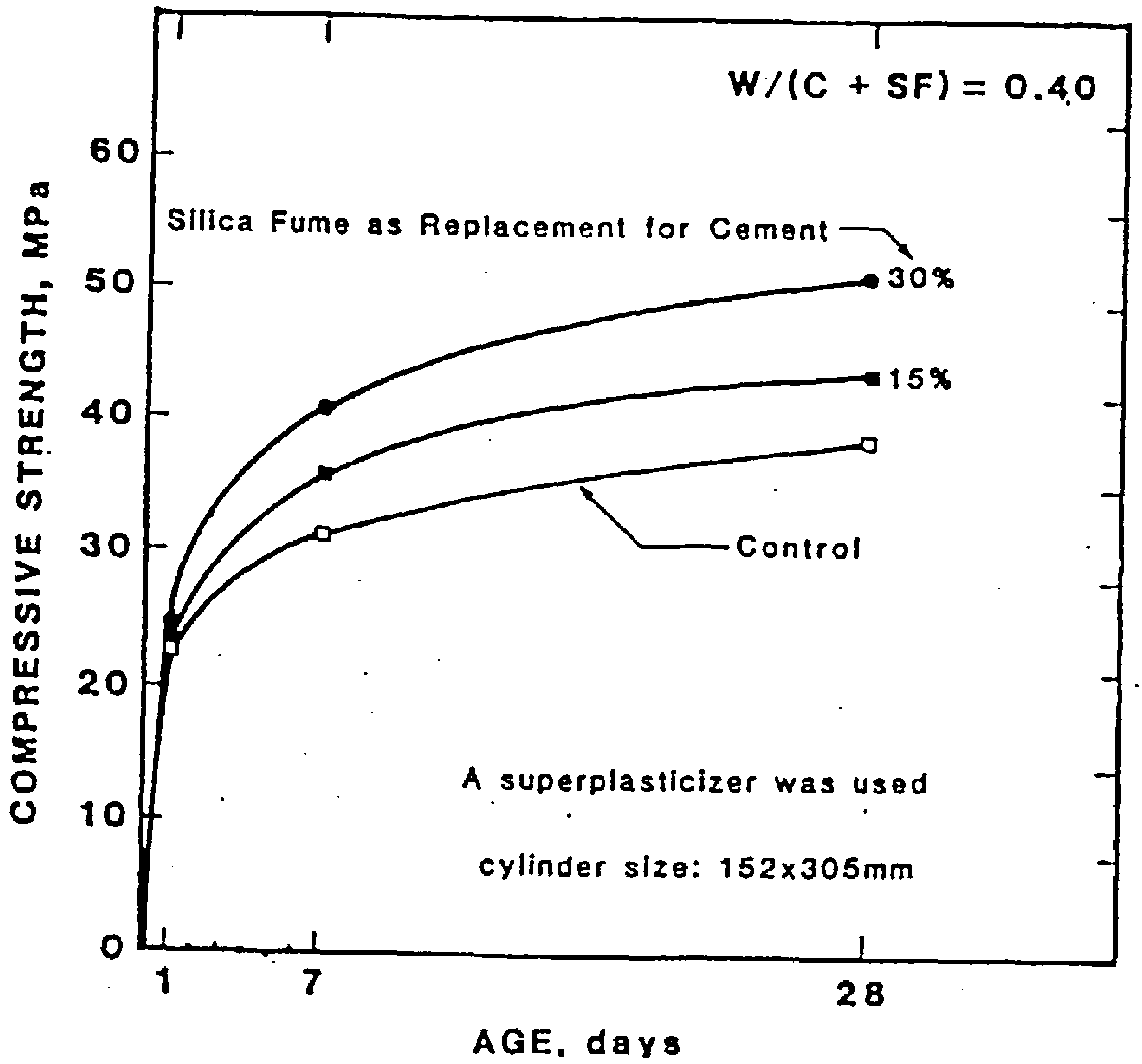


Figure 2.7 Effect of silica fume on strength of concrete [38].

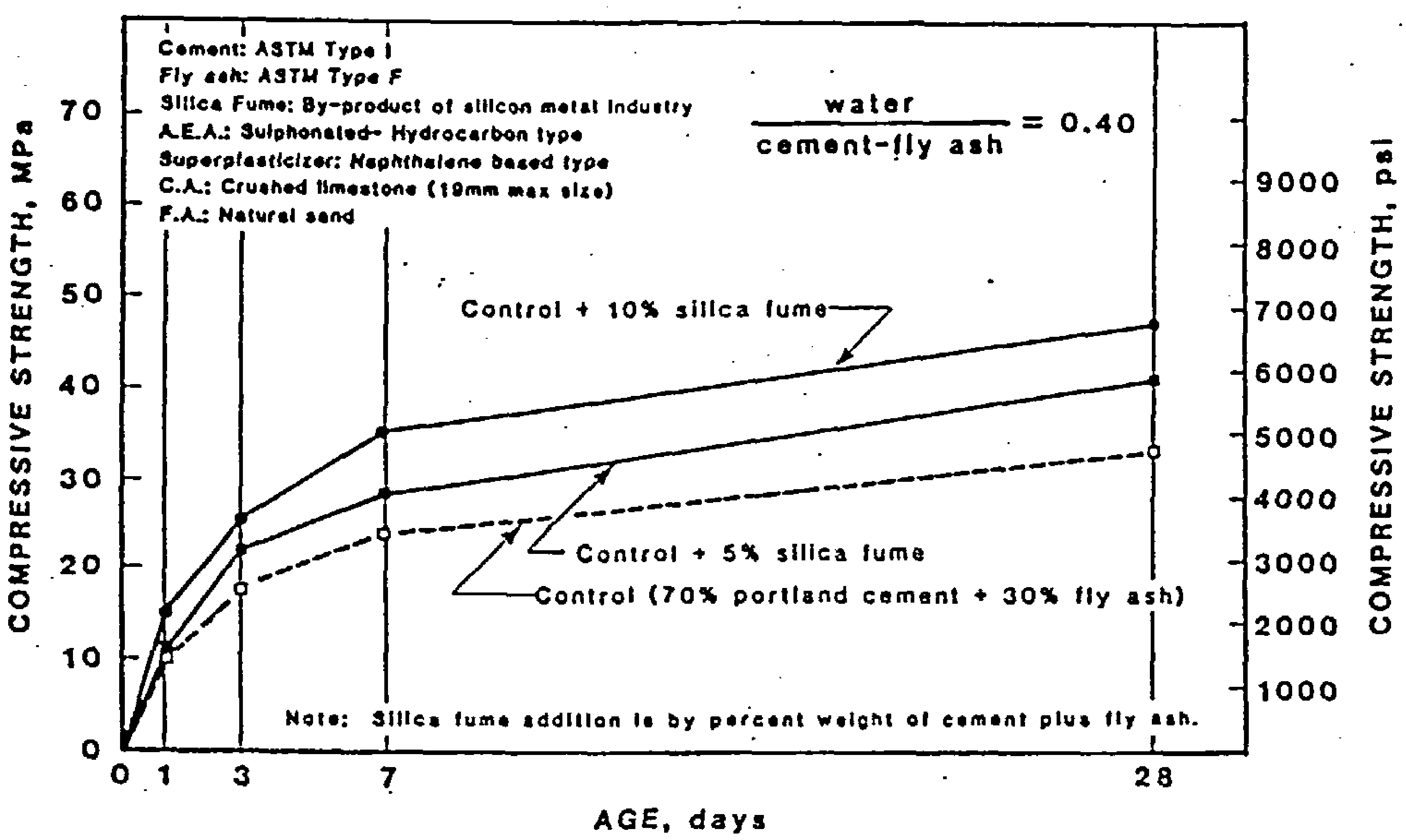


Figure 2.8 Effect of silica fume on strength of concrete with fly ash [38].

Regourd et al [46] reported that at early ages, blended cement mortars with 30% hydraulic slags or pozzolans have lower mechanical strengths than mortars incorporating 100% portland cement. They studied the action of 5% SF replacement for slag or pozzolan from 7 days to 3 months by measuring the mechanical strengths of the mortars. They concluded that with slightly or slowly reactive pozzolans such as FA mechanical strengths and microporosity of mortars improved at 28 days, and that with slag the improvement is more marked in Figure 2.10. This is due to the formation of dense C-S-H, strong cement paste-aggregate- bond and increase in mechanical strengths of the order of 20% [46].

Several other investigations [36,46] using the similar approach, have explored the possibility of using SF in combination with FA. The purpose has generally been to use the highly reactive SF to compensate for the slow strength development associated with FA in concrete. Their results confirm this possibility. Work in this study would be carried out to enhance the low earlyl-age strength and other durability properties of a portland cement concrete containing slag or FA by simultaneously incorporating SF.

2.3.4 Modulus of elasticity

The dynamic modulus of elasticity is an important property of engineering materials. It is obtained from vibrational method of testing. The dynamic modulus in itself is not used in design: however, its importance is derived from the fact that it can be measured quite accurately using non-destructive tests, and it has been successfully correlated with other strength variables [47].

The great advantage of this test, apart from its non-destructive nature, is that it is directly related to the internal structure of the concrete [48]. Another advantage is the ability to measure the concrete strength development with time in situ and in laboratory specimens with very small statistical variability.

In fact dynamic modulus of elasticity exhibits a very high sensitivity in reflecting the internal changes in the structure of different cured concrete. The adverse internal microcracking due to prolonged drying thus decreases the dynamic modulus of elasticity of concrete.

The results of modulus of elasticity in 50 to 65% slag concrete presented by Swamy and Bouikni [19] showed that the highest values of elastic modulus are obtained under continued wet curing; with age, increases of 12 to 15 percent are achieved for a strength increase of 25 percent. On the other hand, air drying with no water curing produced

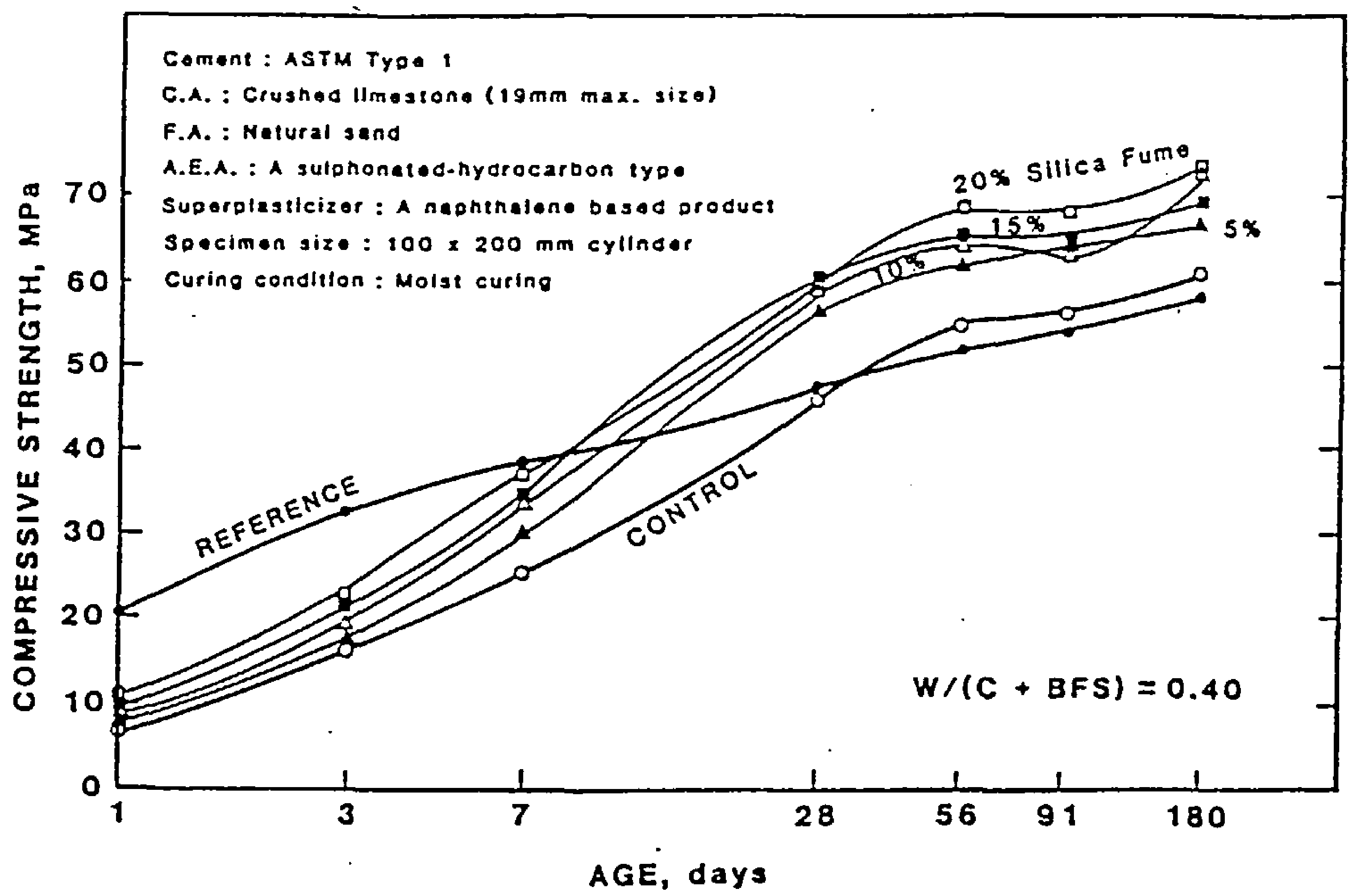


Figure 2.9 Compressive strength versus age for concrete with water/binder of 0.4 [42].

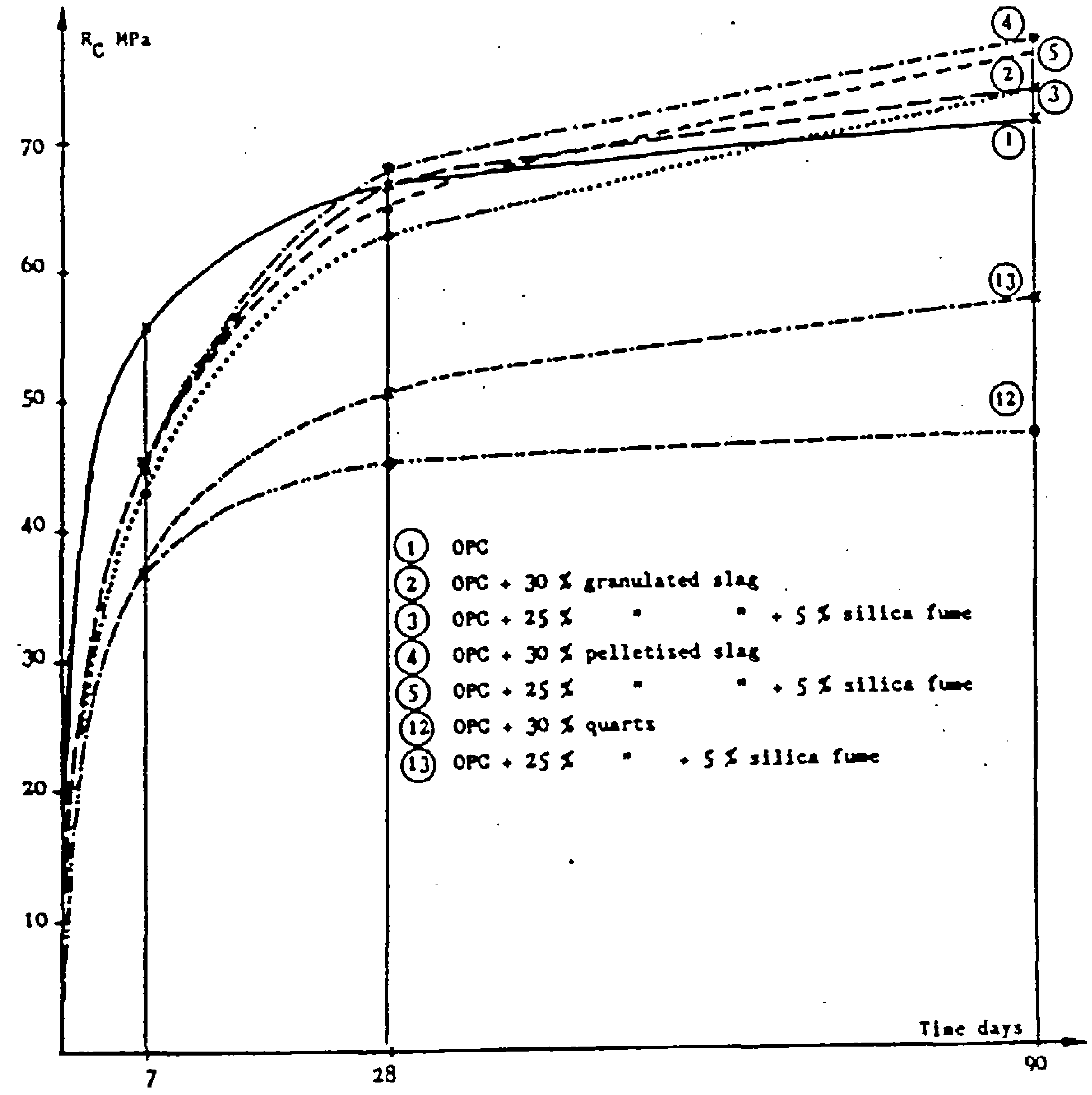


Figure 2.10 Compressive strength of mortars blended cements with slags or quartz and without silica fume [46].

increase of 25 percent. On the other hand, air drying with no water curing produced significant reductions in elastic modulus of about 20 percent within 28 days. With 7 days of initial wet curing, the loss in modulus was restricted to about 15 percent. With continued air drying to 6 months, there was little change in the elastic modulus, although there was a discernable indication of loss in elastic modulus with prolonged dry storage. They [19] also concluded that prolonged drying can create adverse internal microcracking that may not be readily indicated by compressive strength values. Regarding the effect of cement replacement materials on the modulus of elasticity, they reported that under wet curing, there is little difference in elastic modulus between slag concrete and OPC concrete. Results of work carried out by Stutterheim [49] using concrete of 50% cement replacement with slag, showed there to be no significant differences between the OPC and OPC/slag concretes.

It is well known that under wet curing conditions, the dynamic modulus of concrete or mortar increase with age. Swamy and Rigby [48] reported results on an investigation on dynamic modulus of hardened paste, mortar and concrete. They found that the greatest increase, as much as over 100 percent, occurs between 1 and 7 days; the increase beyond 7 days is more gradual and much less varying between 10 and 25 percent, and is of the same order of magnitude as for pastes. At the age of 56 days, many specimens were still showing small increases in the elastic modulus.

In fact the process of drying usually decreases the dynamic modulus and with continued drying the dynamic modulus tend to decrease with age. In general, in differences in dynamic modulus between wet and dry specimens appear to be greater for mineral admixtured concrete than for the corresponding OPC concrete.

During the rapid drying stage-which corresponds to the removal of moisture from capillary channels-there is a rapid decrease in the dynamic modulus, particularly in Young's modulus, which shows down as the rate of differential shrinkage cracking stabilizes [48].

Al-Mudaiheem [50] reported results of an investigation into the influence of drying and wetting on changes in weight and dynamic modulus of paste and mortar specimens dried at different relative humidities at room temperature. He found that drying causes a significant drop in the dynamic modulus due to moisture stress gradients and the removal of the interlayer water caused by drying at low relative humidities.

In another study, on the effect of drying in several environmental conditions on the dynamic modulus of concrete containing superplasticisers, Al-Mudaiheem et al [47] found that there is an increase in that dynamic modulus upon continuous curing underwater, and as the drying temperature is increased the drop in the dynamic modulus of elasticity is increased.

Mehta [34] concluded that the elastic modulus creep, and drying shrinkage characteristics of concrete are not directly influenced by the incorporation of a mineral admixture into a concrete mixture. Instead, these proporties of concrete are largely influenced by the aggregate (both content and stiffness) and by the concrete strength (W/C curing) [34]. It can be said, therefore, that to the extent the strength development in concrete is affected by the incorporation of mineral admixture, its modulus of elasticity will also be affected. In general, when the strength is reduced, the elastic modulus is also reduced. For example Lane and Best [51] found that compared to plain Portland cement concrete, the modulus of elasticity of 25% FA concrete was lower at early ages but slightly higher at 90 days.

For a given 28-day standard-cured design strength, Ghosh and Timusk [52] showed that the modulus of elasticity of FA concrete was generally similar to the reference concrete for all strength levels. Other researchers [11,53] showed that when FA concrete is proportioned for equivalent 28-day standard-cured strength, then FA can be assumed to have no significant effect on the development of its modulus of elasticity.

In regard to slag, at 50% cement replacement levels in concrete mixtures, proportioned to have 45MPa compressive strength at 28 days, Wainwright and Tolloczko [54] found that the 7 day elastic modulus for the slag concrete was 28.5GPa compared by 36.0GPa for the reference concrete (without slag), however at 31 days both were in the 38GPa range, and thereafter only a small increase was observed in the specimens tested at 56 and 171 days. Malhotra et al [55] data show that with 47MPa (28-d) concrete mixtures, both with and without 50% slag replacement, the addition of 5, 10, or 15% silica fume to the slag-cement concretes did not make any difference to the values of the elastic modulus at 28-d, which remained in the 36GPa range.

Sellevold and Nilson [36] in their art report reported that Loland gave modulus of elasticity versus compressive strength data for a large number of concretes, and he found no significant difference between SF and control concretes.

From the above discussion the following can be said:

- The relationship between elastic modulus and age is similar to that of compressive strength and age i.e. the modulus of elasticity increased with age, paralling the compressive strength development.

- When comparisons are made on the basis of equal compressive strength the addition of slag lead to similar modulus values to that of OPC concrete.

- Slag cement concretes develop their modulus more slowly than do equivalent OPC concretes; the higher the slag content, the slower the rate of gain of modulus at early ages.

- Compared to OPC concrete, both compressive strength and modulus for the concrete containing FA are lower at early ages but equal at later ages when FA concrete developed hgher strength.

- In SF concrete mixtures designed for high strength, the elastic modulus do not increase significantly with increasing compressive strength.

2.3.5 Drying shrinkage

Shrinkage is caused by loss of water by evaporation or by hydration of cement, and also by carbonation. The reduction of volume i.e. volumetric strain is equal to 3 times the linear contraction, and in practice, shrinkage is measured simply as a linear strain; it is thus dimensionless and is usually expressed in micro strains 10^{-6} [3]. The conditioning of the test specimen before the beginning of drying shrinkage seriously affects the test results [56]. Several investigators have reported data on the shrinkage of SF, FA and slag concretes [19,36,39,57,58], but test results are generally difficult to compare because of the different mix proportions, the different curing conditions and curing periods used before shrinkage measurements; also, most of these published data are limited to the incorporation of one cement replacement material only.

In those cases where the addition of FA increases the paste volume, drying shrinkage may be increased slightly if the water content remains constant; but if there is a water-content reduction, shrinkage should be about the same as concrete without FA [40]. Davis et al. [59] studied different FA-cement mixtures and found no apparent differences in drying shrinkage between concrete with up to 20% FA content and non-FA concrete. Mehta [34] reported that in well-cured concretes incorporation of up to 25% FA did not have any significant effect on the drying shrinkage. Using a low-calcium FA, Munday et al. [60] found little difference between the drying shrinkage values of several control concretes (without FA) and FA concretes. Again this is true if a proper curing regime is employed. Lane and Best [51] arrived at a similar conclusion and reported that the drying shrinkage of plain and FA concrete prisms was essentially the same after 40 years. It seems that the replacement of cement by FA has little influence on the drying shrinkage property of the concrete. This might be due to the reduction of water demand in FA mixes.

When the cement replacement level is high, for example, in a slag concrete containing 50% slag by weight of total cementitious solids [61], the drying shrinkage was signficant, higher than the control concrete (without slag), and the long term shrinkage of concrete with 65% slag replacement is thus likely to be much higher than that with lower slag replacement. Swamy and Bouikni [19] reported that when subjected to continuous drying, concrete with 50% slag has initally higher shrinkage than with 65% lag up to about 6 months. It is believed that the increased shrinkage may be due to the greater volume of paste in the concrete when slag is substituted on the equal mass basis [41]. The addition of gypsum to the slag will reduce the shrinkage much the same as with portland cement [61].

The data from drying shrinkage tests show that the long-term shrinkage of concrete is not affected significantly by the addition of SF, especially when the water content of the concrete mixture has not been changed [11].Carette and Malhotra [62]reported that upto 84 days of test period the drying shrinkage of concrete prisms incorporating 0 to 30% SF was generally comparable to that of control concrete regardless of the water/binder ratio.

2.4 Durability

2.4.1 Permeability; effect of curing and cement replacement materials

The performance of concrete depends on its quality and the aggressiveness of the environmental conditions. Concretes containing mineral admixture such as FA, slag and SF are acknowledged to have a higher resistance to chemical attack by aggressive environments than do portland cement concretes. Provided the concrete mix is proportioned well and the concrete cured adequately, its quality determines its time dependent resistance to environmental attack and is dependent on the strength of concrete and its permeability to the ingress of harmful agents such as moisture, oxygen and carbon dioxide gases and chloride and sulphates ions.

Mehta [1] defined the permeability as the property that governs the rate of liquids or gases travel through the concrete as a result of a difference in pressure or concentrations. In fact the penetration of liquids or gases can take place through the concrete only if at least some of the pores are interconnected. This means that permeability of concrete is related by its porosity and pore size distribution. It can be said, therefore, that the performance of concrete under a particular environment cannot be soley related to its strength but that it is a function of its pore structure and permeability [2,17]. In reference [2] Cabrera reported that "the new British code of practice for the structural use of concrete [17], for example, specifies strength, cement content and water/cement ratio as a criteria for design. This, although not satisfactory, is an attempt to control performance by directly controlling porosity. The new draft for the Eurocode [63] in concrete has, however, proposed the, measurement of permeability as sole criterion for durability". In recent years a large amount of work has been devoted to this problem [13,9,64], however, there is no accepted method for measuring permeability [2].

The majority of work carried out on the permeability aspects of high performance concrete investigates the effect of one cement replacement material (FA or SF or slag), and there is little published data on the influence of SF, in combination with FA or slag as a replacement material on the permeability. It is suggested that when SF is added to FA or slag to produce high early-age and long-term strength concrete then one would expect that the pore structure and impermeability would be improved, and hence the durability.

Celik [65] reported laboratory investigation of low-permeability concretes with combinations of OPC, slag and SF. He concluded that:

I. the use of slag as a portion of the cementitious material in concrete results in a product with an appreciably lower chloride permeability than similar concrete with only portland cement as the cementitious material. The addition of silica fume to such slag concrete further reduces the chloride permeability. Concretes containing as much as 47 percent slag as low as 3 percent silica fume can develop a low chloride permeability within 28 days at a w/c of 0.40,

II. when concretes with or without slag and silica fume are stored outdoors for 1 year, in a mild climate with moderate rainfall, a large reduction in permeability occurs, and

III.curing concretes containing slag and SF at a temperature that is higher than room temperature for some initial curing period is beneficial in that a lower permeability will be developed within 28 days .

Celik and Woodrow [66] reported an investigation on an improved concrete quality with combinations of FA and SF. The effects of different curing temperatures and different durations of moist curing were also determined. They concloded that adding relativety small amount of SF to FA concretes with w/c of 0.40 to 0,45, results in concretes with satisfactory strengths and very low permeabilities at 28 days. They concloded also that with concretes containing a combination of FA and SF, increasing the early curing temperature (up to 38 C) and duration of moist-curing reduces the chloride permeability.

Curing conditions greatly affects the air permeability of concretes and the real dangers of inadequate curing i.e. with the blended cements.

Graf and Grube [25], have reported that slag concrete can have lower permeability than equivalent OPC concrete with good curing, but a higher permeability when curing is poor. It has also been reported [41,67] that as the slag content increased, the permeability of concrete decreases. This is the result of improvement in pore structure, and substantial curing periods are recommended if this pore blocking process is to be realised with slag and FA partial cement replacements [68,15].

Dhir [11] reported that, where a method of simple partial replacement of portland cement by FA is adopted, this may give rise to a higher permeability at early ages, although with time the position will reverse. However, when FA concrete is proportioned to achieve a specified workability and 28-day strength equal to that of a portland cement concrete, the permeability should also be expected to be similar, as can be seen from the initial surface absorption test and air permeability test results shown in Figure 2.11 [11].

Sellevold [36] cited Hustad and Loland work on the permeability of concrete containing SF and concluded that there is a significant effect on permeability. For example, a concrete mixture containing 100kg/m^3 portland cement, 20% SF, and superplasticizer showed approximately the same permeability as a concrete containing 250kg/m^3 portland cement but no SF or plasticizer.

Ramezaniapour and Malhotra [43] work on effect of curing on the compressive strength, resistance to chloride-ion penetration and porosity of concretes incorporating FA, slag and SF show that, the reduction in the moist-curing period results in lower strengths, higher porosity and more permeable concretes. Under continuous wet curing the control and 25% slag concretes showed high permeability, whereas the concrete containing 50% slag and 25% FA or 10% SF show low permeability values. On the other hand, under air

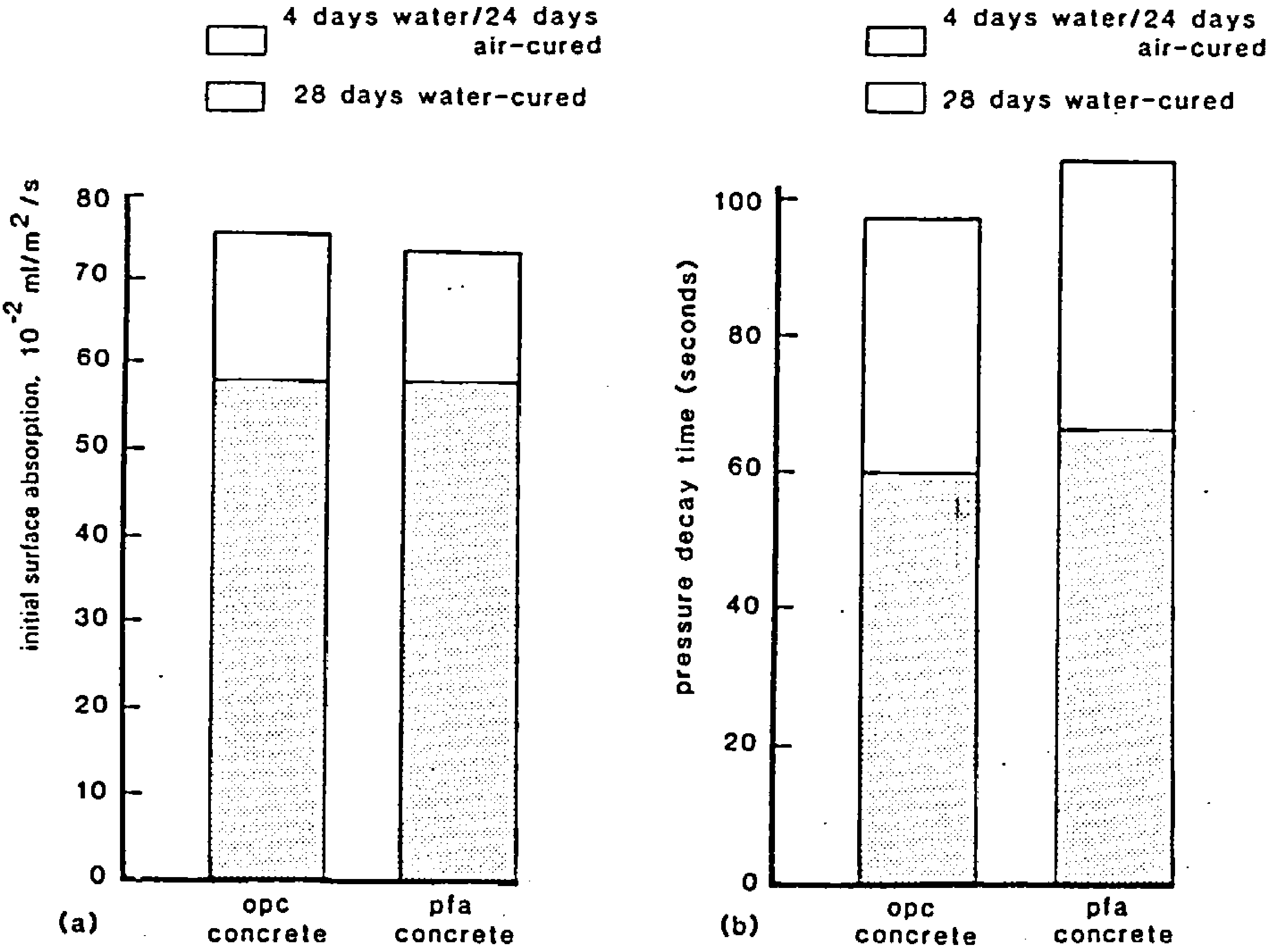


Figure 2.11 Comparison of the permeability of concrete with and without fly ash. a- initial surface absorption; b- time taken for a fixed air pressure decay [11].

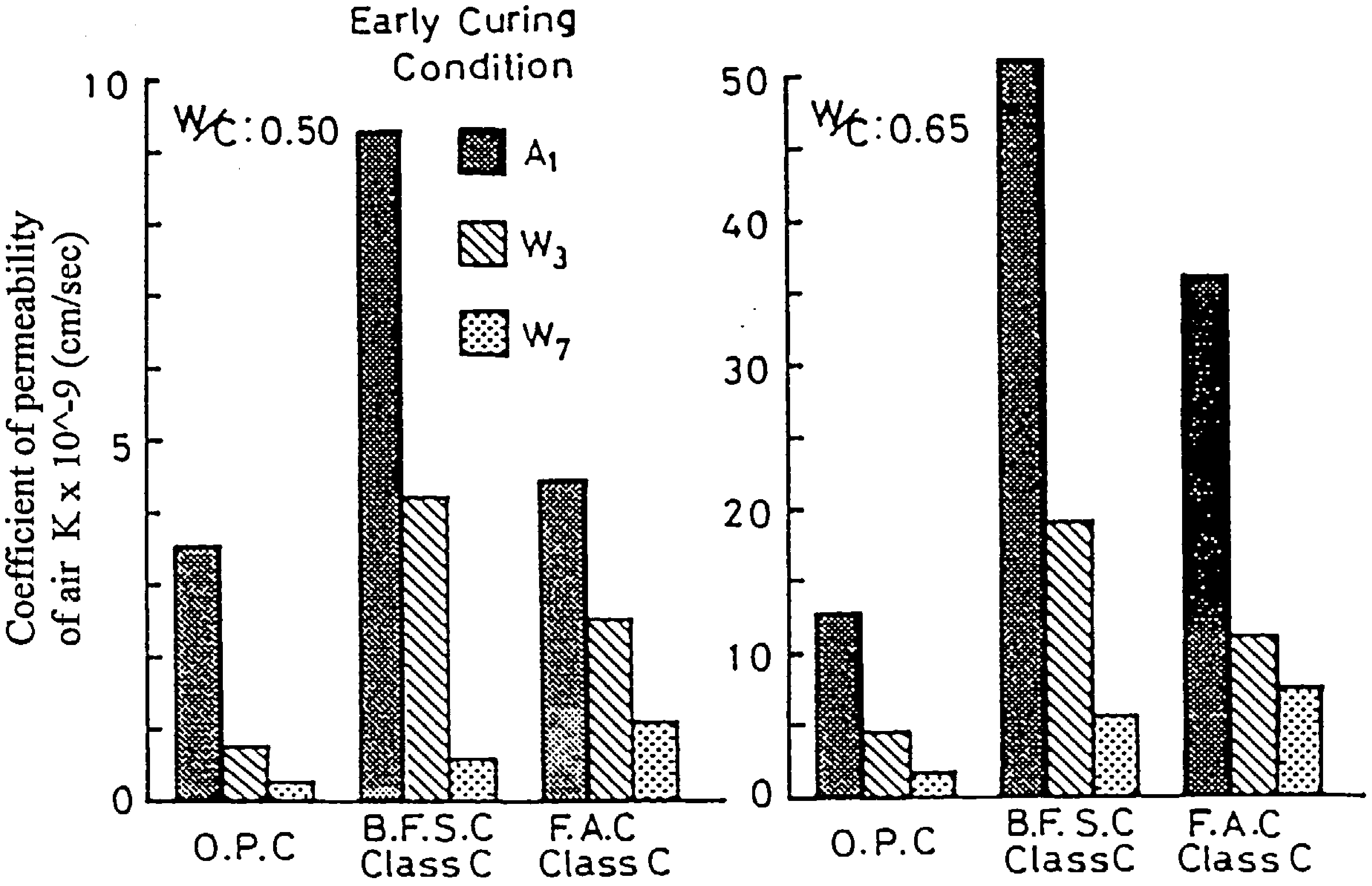


Figure 2.12 Relationship between early curing condition and coefficient of permeability of air at six months (difference of air pressure:2x10^5 Pa)[69].

curing, 2 day moist curing and curing at 38°C and 65% RH, regardless of the age, the concretes investigated exhibited very high permeabilties.

The high permeability of the concretes indicated by the test results of Ref [43] could be due to the lack of the moisture availability of the hydration of the cementitious system, thus the need for long moist curing is a necessity.

The effects of blended cements, curing conditions and age on air permeability were studied by Kasai et al [69]. Figure 2.12 shows their results. They found that:

I. the permeability increases with age because specimens were dried more,

II. the air permeability of blended cements was greater than that of portland cements, the higher the content of FA or slag in cement the greater the coefficient of permeability was, and

III. when the early moist curing was carried out for longer periods the permeability becomes lower, because the cement paste of mortar was hydrated more resulting in more compact matrix.

Lynsdale and Sit [70] reported that air curing adversely effects the air permeability of concrete and the effect is more detrimental for OPC/FA and OPC/slag concretes than for OPC concrete. They found that with the exception of slag mix, oxygen permeability did not reduce with age for air cured specimens. This was in contrast to their compressive strength results where it was found that air curing did not affect strength gain during the early ages. This means that early age strength and its development are not influenced by the type of curing, whereas permeability is much affected. Lawrence [71] stated that the most important parameters controlling gas permeability are the relative humidity and degree of curing of the concrete. He also found that the oxygen permeability increases with drying (age) for OPC and blended cement concretes.

However, the above discussion indicated that continued exposure to a drying environment of inadequately cured blended cement concrete can adversely effect its permeability and thus its long-term durability. Also, the continuous moist curing of concrete is essential to achieve lowest permeability and to realize the all benefits of FA, slag and SF replacements.

2.4.2 Porosity and pore structure; effect of curing and cement replacement materials

One of the most important properties of mineral admixtures when used as replacements with portland cement, is their ability greatly to reduce the porosity and refine the pores, and thereby improvement of durability properties. Open pores, can permit the passage of aggressive agents and lead to deterioration of concrete by corrosion so, the size of the pores their extent and shape are very important factors in deciding the suitability of concrete for construction applications. The determination of pore structure properties is, therefore, a vital step in the evaluation of concrete performance.

Manmohan and Mehta [72] have demonstrated a relationship between pore structure, permeability, and durability of blended cements. Mehta and Manmohan [73] from an investigation on the pore size distribution and permeability of portland cement pastes hydrated with different water/cement ratios, found that the pore size distribution data, rather than total porosity, provides better opportunity for developing accurate correlation with permeability. This is because the large pores have a greater influence on permeability than the small pores. They [73] concluded that irrespective of the age of hydration and water/cement ratio, as long as specimen of hardened paste did not contain pores greater than 1320A its permeability remained insignificantly low. They also found that with increasing age of hydration there was reduction in the threshold diameter, and the cumulative volume of pores.

Day and Marsh [74] reported an increase in intruded pore volume when 30% of cement is replaced by FA, but pore size distribution had been altered to finer pores. Mehta and Gjorv [45] measured pore structure by mercury penetration method cement pastes with water/cement ratio = 0.74 and in equivalent pastes where 30% of the cement volume was replaced by FA, SF or an equal volume of two. The results showed that at 90 days the total penetration was equal for the control and the SF pastes. In parallel investigation on concrete mixes with same proportions they concluded that from stand point of early concrete strengths, it is better to used mixture of low and high surface-area such as FA and SF, than using a normal pozzolan only. In this approach reduction in the volume of large pores (>0.1μm) was observed with the progress of the pozzolanic reaction.

Slag is, in a way simliar to FA. Bakker [75], Roy and Idorn [76] suggested that the pore structure of concrete containing slag is changed through the reaction of slag with the calcium hydroxide and alkalis released during portland cement hydration. Pores in concrete, normally containing calcium hydroxide, are then in part filled with calcium silicate hydrates resulting in reduction in the total pore volume and pore size [75-77]. Based on Roy and Parker [78], where slag is used reduction in the pore size has been noted prior to 28 days after mixing. The volume of pores decreased from about $0.22cm^3/cm^3$ for portland cement paste to about $0.17cm^3/cm^3$ for 40% slag 60% cement paste. This is conditioned by adequate curing.

SF is not quite similar to FA or slag. It is highly pozzolanic compared to FA or slag. When used in a cement system, it leads to a reduction in calcium hydroxide content which is consumed by the reaction with SF. The decrease in calcium hydroxide content is about linear with increasing SF content in mature pastes [79]. The particle-size distribution of a typical SF shows most particles to be smaller than one micrometer (1μm) with an average diameter of about 0.1μm, which is approximately 100 times smaller than average cement particle [38]. Due to the fact that particles are small, silica fume particles act as a filler between cement particles, hence producing a denser mix which reduces bleeding. This would lead to improved pore structure. Feldman and Cheng-yi [80] reported that relatively discontinuous pores are formed in pastes of silica blends after only 7 days of curing, which are related to the consumption of calcium hydroxide crystals by reaction with silica fume.

The pore structure of cement/SF pastes has been studied by Sellevold et al, [79] using different techniques. They concluded that increasing SF dosage at constant water/cement ratio did not change the total porosity, but lead to a refinement of the pore structure.

Ramezanianpour and Malhotra [43] reported data on the effect of curing of the pore structure of concretes incorporating slag or FA or SF. His results show that under continuous moist curing control mix exhibited lowest total porosity. This is followed by 50% slag mix, 25% slag mix, 10% SF mix and 25% Fa mix, in that order. This could be due to that hydration reactions in the case of slag concrete, and pozzolanic reactions in the case of FA and SF concrete proceed at relatively slow rate. On the other hand under continued exposure to drying environment, as expected, all mixes show significantly higher total porosities as compared with the values obtained for continuous moist curing condition. The control mix shows the highest cumulative pore volume percentage of about 35%. The other mixes also perform poorly, with cumulative pore volume percentage in excess of 20%. This shows that moist curing of concrete is essential for refinement of pore structure and for achieving low total porosity.

Mangat and El-Khatib [23] presented results of an investigation to determine the influence of curing on pore volume and pore structure of blended cement pastes and concretes. The cement replacement materials used were FA (22%), slag (40%) and SF (9%). The results show that dry curing at early ages results in higher intruded pore volume, coarser pore structure higher absorption of the surface zone compared with initial moist curing. The affect was more pronounced in FA and slag blended mixes than in control and SF mixes.

CHAPTER THREE

EXPERIMENTAL PROGRAMME AND CHARACTERISTICS OF MATERIALS

3.1 Introduction

In recent years, improvements in concrete properties have been achieved by blending cements with pozzolanic and/or cementitious admixtures such as, fly ash (FA), ground granulated blast furnace slag (GGBFS) and silica fume (SF). Incorporation of these materials in concrete mixes improves the durability by refining the pore structure of the resulting concrete, and thus reducing its porosity and permeability. The movement into concrete of aggressive substances such as chloride ions and carbon dioxide which are the main causes of corrosion of reinforced concrete structures that affect their integrity and long term serviceability life, is thus very much reduced. The surroundings of concrete structures in the Arabian Gulf area are highly contaminated with chloride, sulphate and carbonate salts, and reinforcing bars can corrode before being placed in concrete. In fact deterioration of concrete due to the corrosion of reinforcing steel in the Gulf area appears to be more severe than any other part of the world. For example, in Bahrain 64 pile caps on two bridges, only 20 years old, suffer from severe corrosion due to the ingress of chloride ions from the aggressive marine environment of Bahrain. The deterioration of concrete is not a result of only aggressive agents, but the overall quality of concrete and low cover to steel also play a major role. In view of this problem, various durability studies have recommended blended cement concrete for marine environments; and in recent years blended cement concrete, because of its long term performance, has received considerable acceptance in Bahrain and Gulf countries where a growing number of concrete structures are constructed or under construction with the use of cement replacement materials. Therefore any attempt to alleviate the deterioration-risk implies producing high performance concrete capable of withstanding the harsh environmental conditions. The experimental programme carried out in this study by producing FA/SF and slag/SF concrete would aim to achieve this.

In this chapter, the experimental programme and the materials used together with their properties are described. In the experimental programme, the tests carried out on different concrete mixes, curing regimes, mix proportions and casting of specimens are discussed. In order to minimise the effects of the variation in material quality that gives higher confidence when interpreting the results, strict control over the storage and quality of materials used throughout the whole period of research was adopted i.e. storing them at the same temperature, keeping them sealed in plastic bags and using most of the materials from one batch.

3.2 Purpose and scope

The overall aim of the experimental programme of this research is to produce a workable high performance concrete mix that would provide both long-term and early-high-strength that would meet the durability requirements of most practical constructions in an aggressive environment such as the Gulf area. The important aspects investigated are described below:

1) To develop mix proportions made with varying percentages by weight of cement replacement materials for a 28-day cube compressive strength of about 60 MPa under 7day wet/air curing.

2) To establish the economical and practicable range of combinations of FA/SF and slag/SF that would have good workability (with 100 to 150 mm slumps), high early strength development comparable to portland cement concrete, and a low water/binder ratio.

3) To assess the influence of cement replacement materials on the following properties:

a) Compressive and modified flexural strength, b) modulus of elasticity, c) internal structure through pulse velocity, and d) shrinkage and swelling.

4) To study the effect of different curing regimes with age on the above properties with particular emphasis on 7d wet/air curing.

5) To study the permeability of composite cement concretes by means of gas permeability .

6) To study the porosity and pore structure of composite cement concretes by means of mercury intrusion porosimetry .

7) To examine the existence of possible relationships between pore structure and the above measured engineering properties and gas permeability.

8) To investigate the influence of curing regimes and blended cements on permeability and pore structure.

3.3 Details of the experimental programme

The tests carried out in this study can be broadly classified into three parts, namely: Part I - Mechanical properties of concrete containing various combinations of FA/SF and slag/SF when exposed to different curing environments, Part II - Effect of cement replacement materials and curing regimes on pore volume and pore structure, and Part III - Oxygen permeability at various ages as affected by cementitious replacement materials and curing.

The experimental investigation in the three parts of this study attempts to relate concrete material properties to different environments in order to assess the performance of the concrete mix before it finds its way into many important concrete structures.

Six different mixes were executed for each part. The main elements studied at different ages are (1) three different curing regimes, and (2) three types of cement replacement materials (combination of FA/SF and slag/SF). Properties tested with these mixes as effected by curing are given in Table 3.1.

3.3.1 Detail of mixes

Six different concrete mixes having workability within a given range of 100-150mm slump were adopted in this research.

The mix details used in this investigation are given in Table 3.2. Mixes W, X, Y and Z were made with a total constant cementitous content of 350 kg/m^3. The other two mixes ZX and ZY had a cementitious content of 450 kg/ m^3. These two cementitious contents were selected based on surveys carried out in Bahrain where they are commonly used in the construction industry.

The mineral admixtures were used to replace cement by percentage of cement weight. The percentage of sand in the total aggregate was kept constant at 33% for all mixes, since change of the coarse and fine aggregate quantities would affect the moisture content, and the pore structure measurements of both the mortar obtained from different concrete mixes and the concrete cores tested itself. The air permeability measurements may also be affected. Also, this ratio was applicable to most practical concretes

Table 3.1 Parameters tested in tihis study

Part No	Parameter tested
Part I	Workability Compressive strength Modified compressive strength Flexural strength Dynamic modulus of elasticity Pulse velocity Shrinkage and swelling
Part II	Porosity Pore size distribution
Part III	Permeability

Table 3.2 Concrete mix proportions, kg/m^3

Mix	Cement OPC	Silica fume	Fly ash	GGBFS	Water	Fine aggregate	Coarse aggregate	Superplasticiser *
W	350	-	-	-	157.5	600	1225	1.2
X	300	20	30	-	157.5	600	1225	1.2 - 1.5
Y	250	20	80	-	157.5	600	1225	1.2 - 1.5
Z	250	20	-	80	157.5	600	1225	1.2 - 1.5
ZX	300	25	-	125	202.5	600	1225	0.60
ZY	250	35	-	165	202.5	600	1225	0.68

* superplasticiser:weight % of cementitious contet.
replacement levels:
mixes X,Y,Z & ZX = 6 % SF and for mix ZY = 8 % SF
mix X = 9 % FA and mix Y = 23 % FA
mix Z = 23 % slag, mix ZX = 28 % slag and mix ZY =37 % slag

discussed in the literature when deciding the mix proportions. The aggregate/cementitous ratio was kept at 5.26/1 and 4.06/1 for the 350 kg/m^3 and 450 kg/m^3 mixes respectively. The mix proportions for all water/binder concrete mixes are shown in Table 3.2 . All these concrete mixes had the same water/binder materials ratio (w/b) of 0.45. A superplasticiser was added to all concretes to compensate for the loss in the workability due to the incorporation of cement replacement materials, and it was added as a percentage by weight of cement.

Mix W was adopted as the control mix. No cement replacement material was used in this mix.

In mix X, 20 and 30 kg/m^3 of cement was replaced by SF and FA respectively. Mixes Y and Z had 20 kg/m^3 of cement replaced by SF, and in addition, 80 kg/m^3 of cement was replaced by FA and slag respectively for the two mixes with the total binder content kept at 350 kg/m^3.

Mixes ZX and ZY had cement replacements of 25 kg/m^3 SF + 125kg/m^3 slag and 35 kg/m^3 SF + 165 kg/m^3 slag respectively with the total binder content kept at 450kg/m^3.

1.2% by weight of cement or binder of superplasticiser SP6 (SF concrete admixture) was added to mix W, 1.2% to 1.5% were added to mixes X, Y and Z, and 0.6 to 0.7% were added to mixes ZX and ZY to provide the given workability.

3.3.2 Mixing and casting

The mixing of concrete throughout the research was carried out in a laboratory at 20±2°C temperature. The aggregates were used in an air dry condition, and the water content was checked and adjusted before mixing to obtain saturated and surface dry (SSD) condition. SSD method consist simply of finding the loss in mass of aggregate sample when dried on a tray over a source of heat. The sand should brought to a just free-flowing condition . Mixing was carried out in an ELE 343530 series concrete mixer with maximum mixing capacity 0.06m^3.

To obtain a uniform mix and reduce bleeding the following mixing method was adopted, based on several concrete mixing experiments carried out [19].

The coarse aggregates were first placed in the pan, and approximately one third of the mixing water added. The aggregates and the water were then mixed for approximately one minute to allow the aggregates to absorb water. The cement (including the cement replacement materials) and the fine aggregates were then added and mixed for another

30 seconds. Superplasticiser was added to the remaining water to ensure full dispersion of the 'superplasticiser particles, then the fluid mixture was added slowly to the uniformly mixed materials, and the mixing continued for a further 90 seconds.

Mixing was continued during the addition of water until thorough mixing had been achieved. After mixing, twelve 100 mm cubes and the required number of prisms were cast in steel moulds for each of the mixes considered in this research. Casting was performed in two layers, each layer being compacted thoroughly, without causing segregation, but ensuring the removal of any entrapped air.

Soon after casting and finishing the top surfaces of all specimens, they were covered with polythene sheets and left in the laboratory for 24 hours at 20±2°C temperature before demoulding. For each mix 12 cubes of 100 x 100 x 100 mm and 30 prisms of 100 x 100 x 500 mm, were cast. The cubes were kept continuously in water at 20°C and tested at 1, 7, and 28 days. Two prisms were used for each of the wet, 7d wet/air, and air curing conditions, and they were tested at 1,7,28,90 and 260 days for the various mechanical properties.

For permeability and pore structure measurements two prisms for each mix and each curing condition were cast i.e. 36 of the 100 x 100 x 500 mm, prisms for each testing age for the six mixes were cast.

3.3.3 Curing

After demoulding the concrete specimens were exposed to one of the curing regimes described below. The specimens were in the steel moulds during the first 24 hours after casting, after which time they were demolded and left to continue curing in the same environment (temperature was maintained at 20±2°C and 75% to 90% relative humidity ,R.H.).

The curing regimes were:

1- Continuous moist curing at 100% R.H.(specimens were referred to as wet-cured).

2- Continuous controlled laboratory internal environment at 75-90 % R.H. , i.e. No water curing after demoulding (specimens were referred to as air-cured).

3- Seven days continous moist curing at 100% R.H., followed by exposure to continuous controlled laboratory internal environment at 75-90 % R.H(specimens were referred to as 7d wet/air-cured).

The three curing conditions were chosen to reflect the relationship between laboratory tests and site practice. Continuous exposure to the lab environment (no water curing at all) simulates the extreme case in the site where the formwork is removed very early, at about 24hr, and no water curing takes place. The 7 day moist curing followed by internal lab exposure reflects the normal practice of keeping the form work on for ages up to one week. During the curing period pulse velocity, dynamic modulus of elasticity, shrinkage and swelling were measured daily for the first month and then twice a week.

3.3.4 Preparation of specimens

The specimens used for testing the mechanical properties in part I of this research were 100 x 100 x 500 mm prisms, as stated in section 3.3.2. In some cases 100mm cubes were also tested for compressive strength for comparision purposes. For gas permeability measurement, 50 mm diameter and 40 mm height concrete cores were drilled and cut from 100 mm cube or the 100 x 100 x 500 mm prisms using a diamond saw. The samples were kept wet throughout the cutting process, by dripping water from a reservoir on to the specimen. The specimens were then cut in such a way that the excess of about 10 to 15mm was removed from the cast ends. For pore structure measurements the mortar sample was obtained from the middle (core) of the 100 x 100 x 500 mm concrete prism casted for this purpose. Before permeability or pore structure tests were carried out, the samples were dried in an oven at 105°C for 24 hours to achieve constant weight by evaporating all the moisture content which would effect the flow of gas or mercury through the specimen.

Details of the experimental programme used in the investigation of part II and III are given in Chapters 5 and 6, respectively.

3.4 Characteristics of materials

Details of the materials used throughout the experimental programme are given below. In general the same type of cement, FA, slag, SF, superplasticiser, fine and coarse aggregates were used, although by necessity, some times the materials had to be used from different deliveries. All the constituent materials of the mixes were stored in the lab, where temperature was 20°C ± 2°C.

3.4.1 Cement

The cement used throughout the test programme was ordinary portland cement (OPC).It was obtained from Castle Cement Limited, Lancashire. The chemical and physical properties of the cement are shown in Table 3.3, which were supplied by the manufacturers and complies with the requirement of BS 12; 1991, "specification for Partland cement" .

This cement was supplied inside sealed plastic barrels each weighing approximately 25-30 kg, and stacked in a dry place until it was used for mixing.

3.4.2 Fly ash (FA)

FA is a by-product of the combustion of pulverised coal in power stations. It is a solid material extracted by electrostatic and mechanical means from the flue gases of furnaces fired with pulverised bituminous coal [18]. During production of FA, the coal passes through the high temperature zone in the furnace and the carbon and volatile matter are burned off, whereas most of the mineral impurities, such as clays, quartz, and feldspar melt at high temperature. The fused matter is quickly transported to low-temperature zones, where it solidifies as spherical particles of glass. Some of the mineral matter agglomerates forming bottom ash, but most of it flies out with the flue gas stream and is called "fly ash". This ash is subsequently removed from the gas by mechanical separator, electrostatic precipitators. FA produced in the UK has high glassy silica but low lime content and thus does not react on its own with water, but needs a source of calcium hydroxide before hydrates can be formed(i.e. it is pozzalanic rather than hydraulic). OPC cement is usually used to provide the necessary calcium hydroxide [18].

The suitability of FA depends on a number of factors,two important ones being fineness (45µm residue) to ensure reactivity and low non-reactive carbon content. The FA used in mixes X and Y was obtained from Boral Pozzolan Ltd, Herts. Its main constituents are SiO_2, AL_2O_3 and $Fe_2\ O_3$ with smaller quantities of other metal oxides, as shown in Table 3.3. As the CaO content is 1.38%, it belongs to the low-calcium FA. The MgO content of 1.62%, satisfies the BS3892 Part 1: 1982 "Pulverised Fuel Ash for Use as a Cementitious Component in Structural Concrete", which restricts the MgO content to less than 4%. The chemical composition are shown in Table 3.3.

The fineness of the FA expressed as the mass proportion of the ash retained on a 45µm mesh is 7.6% which satisfies specification BS3892 of not exceeding 12.5%.

Table 3.3 Chemical composition of cement and mineral admixtures (unit:%)

Chemical composition	Cement and mineral admixtures			
	OPC	GGBFS	FA	SF
SiO_2	20.96	34.2	51.4	97.0
Al_2O_3	5.28	11.3	28.1	-
Fe_2O_3	3.14	1.17	11.1	-
CaO	64.35	41.6	1.38	-
MgO	2.59	8.21	1.62	-
SO	3.03	-	-	-
K_2O	0.79	0.40	-	-
Na_2O	0.30	0.26	-	-
TiO_2	-	0.77	-	-
Mn_3O_4	-	0.25	-	-
ZrO_2	-	0.03	-	-
BaO	-	0.06	-	-
C total	-	-	-	0.09
Fe	-	-	-	0.09
Al	-	-	-	0.09
Ca	-	-	-	0.11
Mg	-	-	-	0.09
K	-	-	-	0.30
Na	-	-	-	0.09
H_2O	-		-	0.40
L.O.I.			3.5	1.1
Equivalent Na_2O(%)	0.82			
C_3S	54			
C_2S	19			
C_3A	9			
C_4AF	10			

3.4.3 Ground granulated blast furnace slag (GGBFS)

Blast-furnace slag is a from the manufacture of pig-iron in the blast-furnace, which is defined as a clinker produced in a molten state simultaneously with pig iron in the reduction of iron ore in a blast furnace, and composed chiefly of calcium, magnesium and alumina-silicates [18,81]. The nature of the eventual solid is determined by the way in which the molten slag is cooled. When the liquid slag is rapidly quenched from a high temperature by either water or a combination of air and water, most of the lime, magnesia, silica, and alumina are held in a non-crystalline or glassy state. The water-quenched product is called granulated blast furnace slag, this contains more glass and can be used as hydraulic blinders in addition to portland cement. By drying and grinding to very fine particles, it becomes ground granulated blast furnace slag (GGBFS), and the material will be weakly cementitous and pozzolanic. The chemical composition depends on the raw materials and industrial processes used but should always have a high lime content (49%) when used as a cement.

GGBFS used in mixes was supplied by Civil and Marine Limited, Essex. The fineness of GGBFS was 417m^2/kg which satisfies BS6699:1986 "Ground granulated blast furnace slag for use with Portland cement " which restricts particle size to not less than 275m^2/kg. Its chemical composition is shown in Table 3.3.

3.4.4 Silica fume (SF)

Silica fume, also known by other names, such as condensed silica fume, volatilized silica, or simply as micro silica, is a by-product of the induction arc furnaces in the silicon metal and ferrosilicon alloy industries [81]. Reduction of quartz to silicon at temperatures of up to 2000°C produces SiO vapours, which are oxidised and condense in the low temperature zone to tiny spherical particles consisting of non-crystalline silica. The material removed by filtering the outgoing gases in bag filters possesses an average diameter of the order of 0.1μm and surface areas in the range 15 to 20 m^2/g. Compared to normal portland cement and typical fly ashes, condensed silica fume samples show particle size distributions that are two orders of magnitude finer. This is why on the one hand the material is highly pozzolanic, but on the other it creates problems of handling and increases the water requirement in concrete appreciably unless water reducing admixtures are used. The by-product from the production of ferrosilicon alloy with 50 percent silicon contains a much lower silica content and is less pozzolanic.

The silica fume used in all concrete mixes was obtained from Elkem Materials Limited in slurry form with 50% solids 50% water by weight. The chemical and physical data are given in Table 3.3. It can be seen that the silica fume contains 97% silicon dioxide.

3.4.5 Superplasticiser SP6 (SF concrete admixture)

Superplasticiser according to BS5075: part 3:1985" concrete admixture" is a chemical or mixture of chemicals, in powder or liquid form, which when added to a hydraulic binder content, imparts a very high workability or allows a large decrease in water content for a given workability .

The superplasticiser used in the concrete mixes of this study was a sulphonated melamime- formaldehyde high-range water reducer without chlorides in the form of an aqueous solution. It was obtained from Cormix Construction Chemicals, Cheshire . Cormix SP6 complies with BS 5075: Part I and BS 5075: Part III and conforms to type A, D and G materials of ASTM designation C494.

3.4.6 Aggregates

The fine and coarse aggregates used were washed natural aggregates obtained from the Finningley quarry, Doncaster. After drying, a sieve analysis was carried out on representative samples in accordance with BS812: Part103.1: 1985 "Sieve tests". The sieve analysis results of sand and gravel are given in Table 3.4. The analysis showed that the grading of both aggregates conformed to the limits set out in BS 882:1983 "Aggregates from natural sources for concrete".

The sand had a water absorption coefficient of 1.37%, and a bulk specific gravity of 2.6 in the saturated surface dry condition (SSD) in accordance to BS 812: Part 2: 1975" Methods for Determination of Physical Properties". The coarse aggregate consisted of a mixture of rounded and crushed gravel with 10 mm maximum particle size. The water absorption was 0.80% and the bulk specific gravity was 2.62 in the saturated surface dry condition. The fineness modulus values of the aggregate were 2.12 and 5.75 respectively. The aggregates were air dried before use and stored in plastic drums at lab temperature.

The chemical analysis of sand and gravel using the XRF method is shown in Table 3.5. These results were provided by the aggregate supplier and tested by Whitwell Laboratory. The results shown that the aggregates contained very little

Table 3.4 Sieve analysis of sand and gravel

Sieve size mm	Sand		Gravel	
	Passing %	BS 882:limit	Passing %	BS 882:limit
13.2	-	-	100	100
9.54.75	100	100	92	85-100
2.36	89	89-100	22	0-25
1.18	86	60-100	1	-
0.6	78	30-100	1	-
0.3	32	15-100	1	-
0.15	3	0-15	-	-
F.M.	2.12		5.70	

Table 3.5 Chemical composition of sand and gravel

Mterial:10mm concrete aggregate and washed concreting sand Sourse:Finningley Quarry,Doncaster		
Chemical analysis (XRF method)	Sand	Gravel
SiO_2	93.19	94.12
TiO_2	0.13	0.25
Al_2O_3	2.83	2.48
Fe_2O_3	1.66	1.36
CaO	0.05	0.38
MgO	0.12	0.32
K_2O	1.35	0.88
Cr_2O_3	0.03	0.03
Na_2O	-	0.05
BaO	0.02	0.02
Mn_3O_4	0.01	0.01
Chloride content <0.01%		

chloride(<0.01%)which can be ignored, and the aggregates were considered to be innocuous so far as alkali aggregate reactivity was concerned.

3.4.7 Water

Tap drinking water of the City of Sheffield was used in all mixtures.

3.5 Test details

3.5.1 Workability

Workability of concrete has never been precisely defined. It generally implies the ease of handling, placing and compaction of a concrete with the minimum amount of energy to produce a composite with low porosity and appropriate strength. Therefore consistency, mobility and compactability of a mix have to be considered as the main characteristics.

The workability of fresh concrete was determined by the conventional slump test, described in BS 1881; Part 102:1983," Method of determining slump".

3.5.2 Compressive strength

Modified cube method

The compressive strength of concrete was determined by using parts of the prism tested for modulus of rupture. The end parts of such a prism were left intact after failure in flexure, and since the prism was of square cross-section an "equivalent" or "modified" cube can be obtained by applying the load through square steel plates of the same size as the cross-section of the prism. The test was according to BS 1881: Part 119: 1983 "Method for determination of compressive strength using portions of beams broken in flexure (equivalent cube method). All the compressive results shown in this research was determined by this method.

The strength of a modified cube is approximately the same as the strength of a standard cube of the same size [31], however BS.1881:1952 assumes the strength of a modified cube to be on average 5% higher than that of a cast cube of the same size [31].

Cube tests

A compressive strength test was also performed on 100 mm cubes, at the ages of 1 day, 7 days and 28 days for comparison purposes. The test procedure used was according to BS1881 Part 116: 1983. "Method for determination of compressive strength of concrete cube" Three cubes were tested at each test age and a mean result obtained.

3.5.3 Modulus of rupture

The modulus of rupture was obtained by the symmetrical four-point loading test, which produces a constant bending moment between the load points. The test was carried out according to BS1881: Part 118: 1983, " Method for determination of flexural strength". For each test, two prisms were used.

3.5.4 Dynamic modulus of elasticity

For structural applications and for determining the progressive change in the strength and other characteristics of a concrete specimen, the dynamic modulus of elasticity was measured. The dynamic modulus of elasticity of concrete is related to the structural stiffness and deformation process of concrete structures. It has also been found that the dynamic modulus of elasticity is very sensitive to cracking, which can be used to monitor the effect of drying and in alkali-silica reaction structures.

The instrument used was the "Resonant Frequency Tester", made by C. N. S. Electronics Ltd. The test was conducted by excitation in the longitudinal mode of vibration on the 100x 100 mm end face with a path length of 500 mm. The test principle, procedure and calculation of its value were all according to BS1881: Part 109: 1990, "Recommendations for the measurement of dynamics elasticity".

3.5.5 Ultrasonic pulse velocity

The ultrasonic pulse velocity technique offers an effective means of studying the quality of concrete by monitoring the properties of different concrete mixtures with time and the effect of curing conditions. The technique is very sensitive to the development of internal microcracking.

A commercially available portable equipment (PUNDIT) calibrated at regular intervals was used to monitor the pulse velocity. 54 kHz transducers of 50 mm diameter were used, and the measurements were taken at the centre of the two 100 x 100 mm end faces over a path length of 500 mm. The measurement was made according to BS1881:Part

203: 1986 "Recommendation for measurement of velocity of ultrasonic pulses in concrete".

3.5.6 Shrinkage and swelling

In the present work the changes in length of the 100 x 100 x 500 mm concrete prisms were measured by a commonly used mechanical extensometer of 200 mm gauge length i.e., a "Demec" gauge. Demec points, made of small stainless steel were fixed to the concrete surface along the centre line of the long axis by an adhesive at a prescribed spacing with the aid of a standard calibration bar. The points were fixed on the four sides of the concrete prism. For each mix and curing condition two prisms were used, and initial length measurements were taken immediately after the specimens were demolded.

3.5.7 Pore structure

Porosity and pore size distribution testing of concrete samples was done by mercury intrusion porosimetry (MIP) technique.

3.5.8 Oxygen permeability

Oxygen permeability measurements were carried out, on 50mm diameter and 40mm hight concrete cores, by a new gas permeameter designed by Cabrera and Lynsdale [13].

Details of the procedure of sampling and testing for pore structure and permeability are presented in sections 5.2 - 5.3 and 6.2, respectively.

CHAPTER FOUR

TEST RESULTS AND DISCUSSION OF PART I
ENGINEERING PROPERTIES

4.1 Introduction

Concrete is the most widely used manufactured material in the construction industry. Its the most important property is durability which relates the performance of the material to its service life under various environmental conditions. The ability of concrete to withstand and satisfactorily and for long periods the effects of load, time, and environment depends very much on how the engineering and microstructure properties of the material are constituted initially and how they are allowed to develop with age.

The use of cementitious and pozzolanic siliceous industrial by-products as mineral admixtures in concrete can bring improvements in engineering properties of hardened concrete (strength, elastic modulus, impermeability and general durability) [82]. Normal pozzolan additives due to their low surface area and reactivity are not generally able to improve the early strength which is crucial to the strength and stability of structural concrete applications and durability of concrete. The problem, though, could be solved by using a mixture of normal (such as fly ash and slag) and a highly reactive pozzolan, such as silica fume, to produce a durable concrete which does not suffer from low early strength.

Also the durability of concrete during its service life may be significantly affected by the environmental conditions to which it is exposed, and in order to produce a concrete of high quality, the placing of an appropriate mix must be followed by a planned curing system in a suitable environment during the early stages of hardening. The necessity of curing arises from the fact that hydration of cement can only take place satisfactorily if concrete is kept moist. And with siliceous admixtures, if the pozzolanic/cementious reactions are to be initiated quickly and continue to proceed, and if large and continuous pores are to be reduced to finer and discrete pores, it is necessary that concrete containing siliceous admixtures undergoes curing that is both early and more prolonged than for OPC concrete [39].

Three curing methods were examined in this study, namely : continuous moist curing, continuous uncontrolled internal environment (lab) and 7 day moist curing followed by air curing. These three regimes are considered to reflect the best and worst states of curing and the practices generally followed in the industry.

This part presents and discusses the results of the first part of this investigation on the effect of curing conditions on the engineering properties such as compressive strength, flexural strength, dynamic modulus of elasticity, ultrasonic pulse velocity, shrinkage and swelling of various concrete mixes made with cement replacement materials such as fly ash (FA), silica fume (SF) and granulated blast furnace slag (slag). The results obtained are used to analyse the effect of these cement replacement materials on the above engineering properties. In addition, since strength in compression is commonly accepted as a general index of concrete strength, the relationship between compressive strength and both flexural strength and dynamic modulus of elasticity are discussed.

4.2 Workability

The two basic criteria for mix proportioning concrete containing mineral admixtures to obtain high strength and durability are low water-cement ratio and early and adequate moist curing. Workability cannot, however, be excluded from mix design, particularly for structures with steel reinforcement, since it is misleading to relate workability solely to the water requirements of the mineral admixtures. The workability of all concrete mixes studied in this investigation executed was expressed by its slump; the slump test was performed by the slump cone immediately after mixing the concrete.

It is known that incorporation of mineral admixtures in concrete would lead to a general enhancement in fresh concrete properties that lead to improve consistency, cohesiveness and reduction in bleeding and segregation. The use of FA resulted in mixes having improved workability for the same water/binder ratio, and lower water demand to reach the given slump. This improved workability was not as noticeable in low replacement slag mix and only nominal water reduction was achieved. Different characteristics were observed when silica fume as a third ingredient was incorporated in a given mix; it generally lead to a lower slump, because of its very fine vitreous particles and high surface area. The water reduction associated with the use of fly ash, and generally with the mineral powders, is not solely a mechanical effect, nor is it related entirely to the spherical shape of the ash particles, but the result of dispersion and deflocculation similar to the effect of organic admixtures [39].

From different mixes tested it was found that with the added presence of FA and slag, water demand increased as silica fume was added when no water reducing agent was used. To maintain the same water/binder ratio and the given slump, loss in workability was compensated by the use of the superplastizer.

In fact with blended cements, the use of a superplasticizer is an essential component for mix proportioning. A dosage of 1.2 to 1.5 % by weight of cement (or binder) of superplasticizer SP6 was added to control X, Y and Z mixes, whereas about 0.7% was added to ZX and ZY mixes; this amount of superplasticizer was sufficient to provide a slump of 100-150mm for the control and all other mixes, no segregation was observed. Incorporation of the mineral admixtures in concrete was simply a straight forward replacement of cement, weight for weight. This method results in higher volume of paste with the consequent advantage of improving the cohesion and flow characteristics of the concrete mixture [11].

The results of the slump test are shown in Table 4.1. The table shows that for equal OPC cement content and equal mix water contents, the incorporation of 125 and 165 kg/m3 slag for mixes ZX and ZY reduced the superplasticizer requirement level to the half compared to the other mixes. In other words this increase in powder volume (slag) seems generally of benefit to workability in mixes with low cement contents or when SF is added or where fine aggregates lack some of the finer fractions. However, the improved characteristics on workability by slag are due to (1) its surface texture is much smoother than that of cement, (2) slag has a slightly lower relative density than OPC, (3) particle size distribution of powders (cement and slag), and (4) the increased paste content of the concrete with slag [16,18,41].

Table 4.1 Slump of concrete mixes investegated

Mix	water / binder ratio *	Mineral admixtures, kg/m^3	Superplasticiser, SP6	Slump,** mm
W	0.45	-	1.17	112
X	0.45	20 SF+30 FA	1.35	125
Y	0.45	20 SF+80 FA	1.36	130
Z	0.45	20 SF+80 slag	1.48	105
ZX	0.45	25 SF+125 slag	0.60	115
ZY	0.45	35 SF+165 slag	0.68	110

***binder comprises OPC+mineral admixtures ; ** average**

4.3 Compressive Strength

Strength of concrete is a property generally specified in concrete design and quality control, because it is related to the structure of hardened cement paste [56]; further it can also be related to most other properties .

The compressive strength of the control concrete and concrete with different mineral admixtures was determined by using parts of the prism (100 x 100 x 500mm) tested for the modulus of rupture. They were tested at ages 1, 7, 28, 90 and 260 days, and the results of these tests are shown in Table 4.2. The results show that all the mixes conditioned in the three curing regimens were able to develop the required 28 day strength of 50 MPa; in fact, looking at the results, most of the mixes reached strengths in excess of 50 MPa, about 60 MPa except mixes ZX and ZY without any water curing which showed only 48.6 and 44.4 MPa at the age of 28 days, respectively.

The results show that fly ash or slag concrete with the incorporation of about 6% silica fume can be designed to give a high 28 day strength results. A slight increase of silica fume, say 8 to 10%, can bring a very consistent and high 28 day strength and even a 50 MPa strength at 7 days age, with the same total cementitious content and mix proportioning method that had been adopted. This approach is in agreement with other researchers [34] where they concluded that involving 30% fly ash by weight of total cementitious solids together with varying amounts of silica fume from 5 to 20% when the w/c ratio kept constant by use of plasticer, the addition of SF increased the compressive strength of concrete. This is due to pore size reduction (the filler effect) and pozzolanic activity of the SF which enhance the strengths of the transition zone and the bulk cement paste [83]. The extent of compressive strength increase caused by replacing some cement by SF depends on the age of the concrete, curing conditions as well as the cement and FA/SF or slag/SF contents. Furthermore, the time at which added SF starts to contribute to strength gain depends on w/(c + SF + FA or slag) ratio and cement content.

4.3.1 Early age strength gain (less than 28 days)

Early strength development is of important concern to the construction industry especially when forms are removed early within one or two days, and closely related both to the performance and economics of concrete at early ages. It is critical to the strength and stability of structural concrete applications and should therefore be a prime consideration in mix proportioning [39]. The early gain of strength depends upon the

Table 4.2 Results of compressive strength tests

Mix, type, kg/m^3	Age, day	Compressive strength, MPa		
		Wet	7d wet / air	Air
350 OPC (W)	1	27.3	27.3	27.3
	7	47.5	48.3	46.8
	28	55.7	57.9	52.9
	90	60.8	63.2	59.6
	260	68.5	71.5	62.2
300 OPC +20 SF +30 FA (X)	1	24.0	24.0	24.0
	7	45.7	45.5	45.1
	28	60.1	63.6	60.1
	90	75.5	77.3	71.1
	260	78.3	80.1	73.0
250 OPC +20 SF +80 FA (Y)	1	18.1	18.1	18.1
	7	40.8	41.0	40.4
	28	59.4	64.0	57.1
	90	67.8	72.7	61.0
	260	71.4	76.2	63.0
250 OPC +20 SF +80 Slag (Z)	1	15.6	15.6	15.6
	7	48.6	48.6	46.5
	28	67.9	70.9	61.7
	90	74.8	78.4	67.5
	260	84.8	88.0	70.1
300 OPC +25 SF +125 Slag (ZX)	1	-	16.7	16.7
	7	-	39.6	38.6
	28	-	62.1	48.6
250 OPC +35 SF +165 Slag (ZY)	1	9.6	9.6	9.6
	7	36.6	36.6	36.1
	28	61.6	61.0	44.4
	120	69.7	72.1	52.0

concrete temperature, the moisture condition the mix proportion, (in particular the water/cement ratio) and the quantity, types and sources of materials [18].

For sound basis of comparison all the concrete mixes had the same temperature and moisture condition, besides the same quantity and type of materials were used, from one source. The water/binder ratio for all mixes was held constant by the use of a superplasticser, for the evaluation of the effect of silica fume incorporation and the strength comparisons between concrete mixtures with silica fume and the control (without silica fume). The use of a water-reducing admixture was in agreement with the general practice and recommendations by other researches when more than 5% silica fume by weight of cement is used.

Early age strength comparison with OPC mix

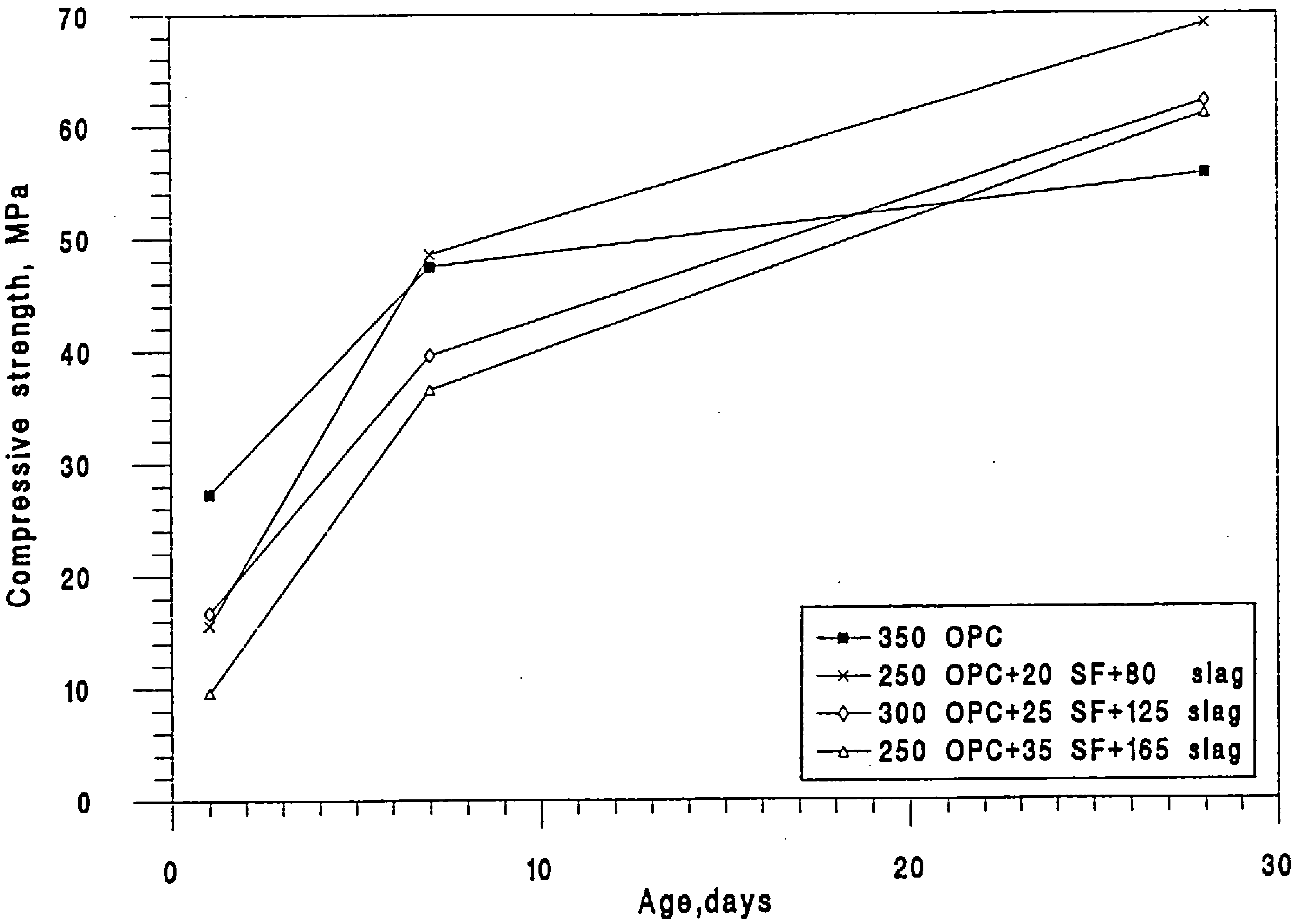
Tables 4.3 and 4.4 present the early-age strength development for water cured of FA/SF and slag/SF concretes respectively. In all concrete mixes, despite the influence of various curing regimes, the early strengths were lower than 350 OPC mix (W) except mix 250 OPC + 20 SF + 80 slag (Z) which showed similar strength at the ages of 7 days to that of OPC mix. Figure 4.1-a shows the pattern of strength development for slag concretes for mix designs which have 350 & 450 binder content and equal workability. For mix 250 OPC + 20 SF + 80 slag (Z) using 23% Slag, the one day strength was about 60% that of OPC concrete and at 7 days the strength was 102% of the control mix, which means that the loss in compressive strength of concrete due to the incorporation of slag can be fully compensated for by the addition of about 6% SF (20kg/m^3). On the other hand keeping cement control constant at 250kg/m^3 the increase in slag from 80 to 165kg/m^3 a reduction in compressive strength of 2 and 7 days. Only at 28 days the strength of the 250 OPC + 35 SF + 165 slag (ZY) concrete was beyond the target strength of 50 MPa. However the loss in strength of ZY concrete compared to Z concrete could be compensated by slightly increasing the SF content. Strength of ZY concrete was 6% and 75% that of Z concrete at 2 and 7 days, respectively. In fact the low one day strengths do not necessarily represent the upper limit or an indicative trend to early strength development for these mixes, owing to slow hydration of slag concrete than that of OPC concrete at this age. However the later age strength development of slag concretes was faster than that of OPC concrete, as shown in Table 4.5. The problem of obtaining higher one day strength relative to 28 day strength for SF/slag concretes compared with control may overcome in practical use by using warm concrete or by heat curing, and this is as an advantage in hot countries because of high

Table 4.3 Compressive strength development of silica fume / fly ash concrete at early ages

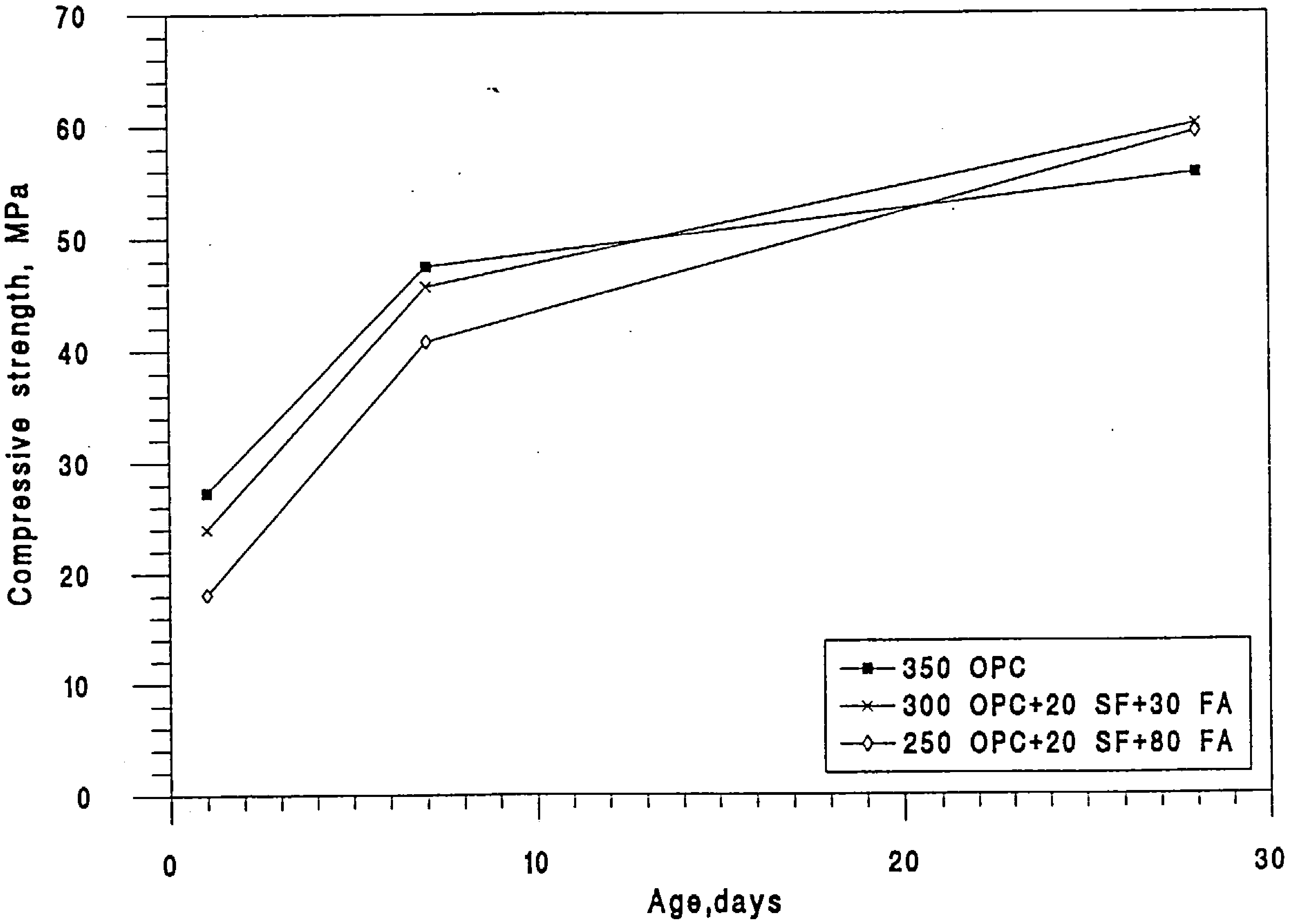
Concrete mixes, kg/m^3	Age, days	Compressive strength, MPa	Percentage of 28 day strength
350 OPC (W)	1 7	27.3 47.5	49 85
300 OPC+20 SF+30 FA (X)	1 7	24.0 45.7	40 76
250 OPC+20 SF+80 FA (Y)	1 7	18.1 40.8	30 69

Table 4.4 Compressive strength development of silica fume / slag concrete at early ages

Concrete mixes, kg/m^3	Age, days	Compressive Strength, MPa	Percentage of 28 day strength
350 OPC (W)	1 7	27.3 47.5	49 85
250 OPC+20 SF+80 slag (Z)	1 7	15.6 48.6	23 70
300 OPC+25 SF+125 slag (ZX)	1 7	16.7 39.6	27 64
300 OPC+35 SF+165 slag (ZY)	1 7	9.6 36.6	16 60



(a) Equal binder content and workability



(b) Equal binder content and workability

Figure 4.1 Early strength gain of slag/SF and FA/SF concretes temperatures. Various researchers [15,36] have shown that strength of slag and SF at high temperatures was improved.

The early rate of gain of strength of concrete incorporating SF and FA results from a combination of factors: high reactivity and fineness of SF and hence an early start of pozzalanic reaction, and increased rate caused by the acceleration of the rate of hydration of the OPC due to the presence of FA. The contribution from the physical and chemical effects of FA in hydrating portland cement concrete starts immediately after mixing , however, its considerable contribution becomes significant at later ages.

The early age-strength development of concrete mixes incorporating SF and FA designed for a same cementitious content, same workability (100 - 150 mm slump) and 28 day standard-cured (20°C water) strength value (50 MPa) is compared with that of the OPC mix designed to the same specifications in Figure 4.1b. This shows no significant difference between 300 OPC + 20 SF + 30 FA (X) and 350 OPC (W) concretes at ages of one day and 7 days (88% and 96% that of OPC mix, respectively) and that strength loss due to FA incorporation was about compensated by addition of 20kg/m^3 SF. About similar age strength relationship has been observed by others [16]. Whereas for FA content of 23%, 250 OPC + 20 SF + 80 FA (Y), the mix gave one and 7 days strength of 66 and 86% of the opc mix, respectively; this indicates that when FA replacement level was increased with same SF content as in X concrete a loss in compressive strength compared to control and X concretes was obtained. However, after 7 days the SF and FA concretes gradually developed higher strength values. In fact the ability of this concrete to produce high ultimate strength can effectively be employed in the production of high strength concrete.

The early age development of strength with respect to 28 day strength, expressed as a percentage of 28 day strength, varies with the replacement levels of mineral admixtures. Examples of such percentages are given in Tables 4.3 and 4.4.

Taking again the two FA/SF ash concretes, with the addition of 30 kg/m^3 FA to the concrete mixture containing 300 kg/m^3 cement caused a strength increase of a 33% and 12% at one and 7 days, respectively, than concrete with 80 kg/m^3 FA addition to the concrete mixture containing 250 cement. At one day, at both replacement levels development was 30 to 40% of their 28 day strength, compared to 49%, for OPC concrete. At 7 days, both FA/SF concretes developed 70 to 75% of their 28 day strength, compared to 85% for the OPC concrete. Carette et al [44] reported that 1 and 3 day strengths for concrete incorporating SF (Figure 4.2) were higher than the control concrete (30% FA, 70% opc) but lower than concrete containing an equivalent amount of portland cement only, and our results is in agreement with this finding. They pointed out also that concretes containing 10, 15 or 20% SF (in addition to FA) were higher in strengths than plain portland cement concrete strength.

With slag/SF concrete mixtures (250 to 300 kg/m^3 cement content), it has been found that the addition of 20kg/m^3 SF to 80 kg/m^3 slag has a better effect on strength development (even at later ages) than is the case with rich concrete mixtures (i.e. >350 total cementious content). With increasing total cementious content (450 kg/m^3), as a result of 23 and 35 kg/m^3 SF and 125 and 165 kg/m^3 slag addition, ZY concrete mixture registered about 40 and 10% lower strength than ZX concrete at 1 and 7 days, respectively. On the other hand comparing ZX and Y concretes of equal cement content (300kg/m3) and SF (5.6%) contents, the concrete containing 125kg/m^3 slag showed about the same 1 and 7 days strength of that of 80 kg/m^3 FA. It can be concluded, therefore, that Slag/SF concretes performed better than FA/SF concretes and that this retardations in one and 7 days strength are primarily a function of the lower percentage of silica fume that was added, and the amount of SF might not be sufficient (at this stage) to compensate for the loss in strength due to slag addition (165 kg/m^3). This loss in strength could be compensated for by addition of as little as 10% SF. A similar approach was taken by Malhotra [55] and a noticeable strength increase was recorded during the early age in moist curing , when most of the pozzolanic reaction takes place [84].

4.3.2 Long-Term Strength Development

The long-term strength development of any portland cement depends on the continuing presence of moisture for hydration [18]. The same can be said for concrete incorporating FA/SF and slag/SF, and where moisture is available and hydration to continue these concretes gain proportionately more strength than does an equivalent OPC concrete.

It is well recognised that addition of SF to concrete provides a significant increase in strength of concrete. SF increases the homogeneity and decreases the number of large pores in cement paste, both of which would lead to a higher strength material [85]. However, the amount of SF replaced and the effect of curing conditions besides the incorporation of other mineral admixtures (such as FA or slag) play a role in development of the strength, and they have to be considered. On the other hand, long-term strength is dependent more on the reactivity of the by-products used. SF (high surface area) is able to make some contribution to the strength of a given concrete

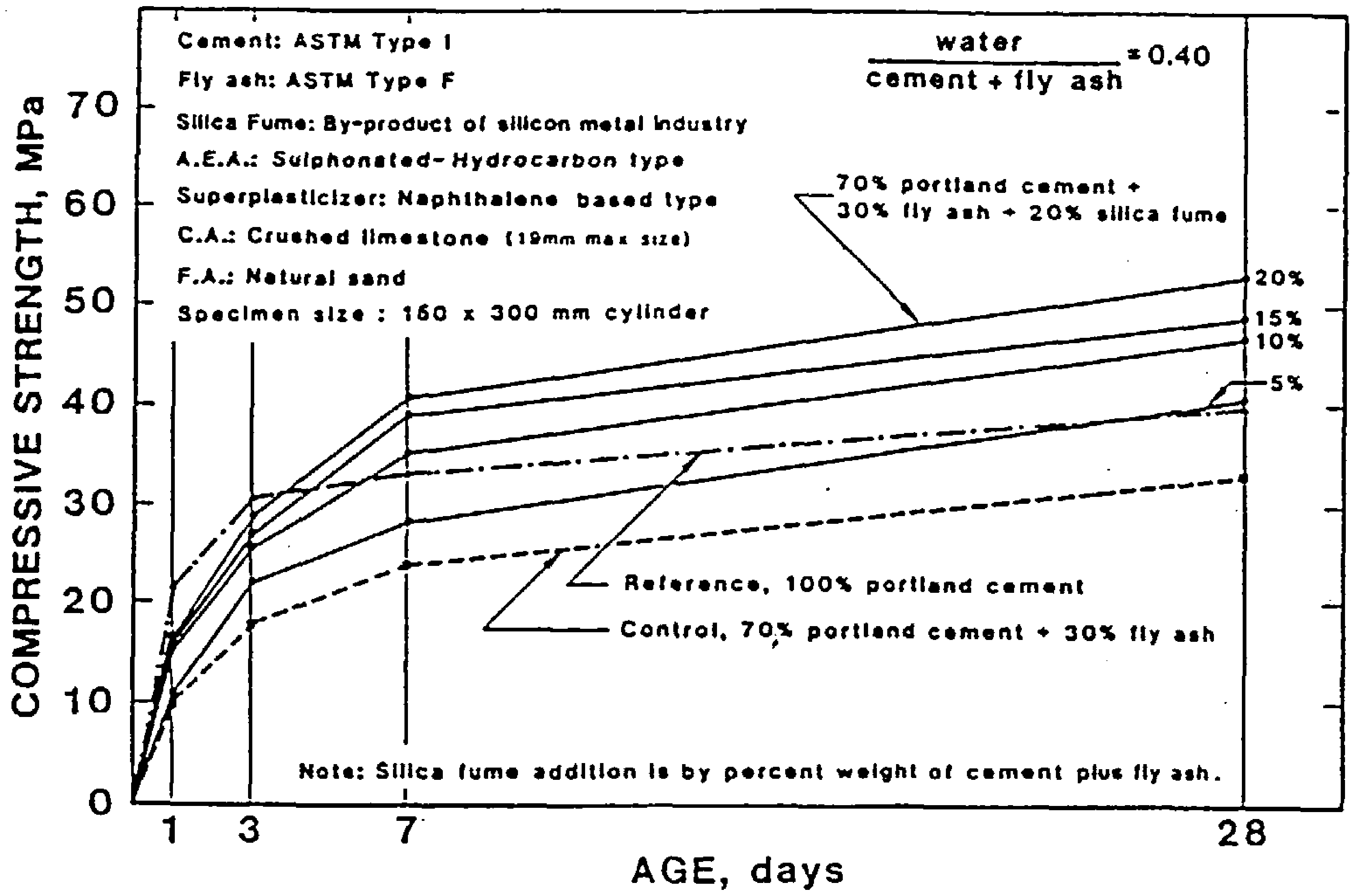


Figure 4.2 Compressive strength versus age for fly ash concretes with a W/(C+F) of 0.45, containing various additions of silica fume [55]. Total cementitious content = 380 to 450 kg/m^3

mixture even at very early ages of hydration (viz, 1 to 3d), significant contribution during the first 2-4 weeks, and relatively little contribution thereafter. FA and ground blast furnace slag, with their much coarser particle size distribution and low specific surface (typically 300 to 500 m2/kg) make little strength contribution at very early ages (up to 3 days), some contribution during the intermediate period (3 to 14 days) and considerable contribution thereafter [34].

The long term strength development of OPC, FA/SF and slag/SF concretes is summarised in Table 4.5 and Figure 4.3 to 4.7 together with the effects of curing conditions on strength development. For the purposes of comparison, the compressive strength at each age of test for each mix is expressed as a percentage of the 28 day strength of the control mix were given in Table 4.6. Each value represents the average of four test specimens. Concrete mixes W, X, Y and Z shown in Table 4.5 are high strength concretes designed for 28 day strengths of 50 MPa with total cementitious content of 350 kg/m^3. Mixture W was the control concrete, without any mineral admixture.

However, from the data presented it can be said that the improvement in strength development brought about by the addition of SF to FA or slag become evident, and beneficial effects on this property can be obtained by utilising FA and slag through correct mix design and proper curing. Also the importance of a minimum 7 day early age water curing for all concretes and its advantages in overcoming strength loss is also shown.

4.3.3 Effect of Curing

The term 'curing conditions' is used to describe the moisture and temperature states in which the concrete is kept after it has been cast [18]. With all cement-based materials, strength development is intimately associated with curing regime, and with materials such as slag, FA and SF, curing takes on a much more important role then with portland cement concrete. With siliceous admixtures that depend on their reactivity to contribute to strength and stability, curing has to be considered as an essential ingredient of the mix design [11,39]. The most critical period of early curing is the first seven days after mixing [34,39,86,68]. The compressive strength development of the concrete mixes for various curing conditions, given in Table 4.5 is confined to curing conditions at 20°C ± 2°C. The results obtained indicate that all 7d wet/air cured specimens exhibited slightly higher compressive strength values ,about 5% higher, compared to wet cured concrete specimens. The slightly lower strength values of wet-cured specimens could be due to 1) the fact there could be some lubrication between the steel platen and concrete surface which cause redistribution of stresses at top and bottom of

Table 4.5 Long term compressive strength development of silica fume / fly ash and silica fume/slag concretes

Mix type, kg/m^3	Age, days	Compressive Strength, MPa		
		Wet	7d wet / air	Air
350 OPC (W)	28	55.7	57.9	52.9
	90	60.8	63.2	59.6
	260	68.5	71.5	62.2
300 OPC + 20 SF + 30 FA (X)	28	60.1	63.6	60.1
	90	75.5	77.3	71.1
	260	78.3	80.1	73.0
250 OPC + 20 SF + 80 FA (Y)	28	59.4	64.0	57.1
	90	67.8	72.7	61.0
	260	71.4	76.2	63.0
250 OPC + 20 SF + 80 Slag (Z)	28	67.9	70.9	61.7
	90	74.8	78.4	67.5
	260	84.8	88.0	70.1
300 OPC+25 SF+125 Slag (ZX)	28	-	62.1	48.6
250 OPC+35 SF+165 slag (ZY)	28	61.6	61.0	44.4
	120	69.7	72.1	52.0

Table 4.6 Compressive strength development expressed as a percentage of 28 day strength of control concrete (W)

Curing condition	Age, day	Percentage of 28 day strength, %					
		W	X	Y	Z	ZX	ZY
Wet curing	1	49	43	32	28	-	17
	7	85	82	73	87	-	66
	28	100	108	107	122	-	110
	90	109	135	122	134	-	125
	260	123	141	128	152	-	-
7d wet / air curing	1	47	41	31	27	29	17
	7	83	76	71	84	68	63
	28	100	110	111	123	107	105
	90	109	133	126	135	-	124
	260	124	138	132	152	-	-
Air curing	1	52	45	34	29	32	18
	7	88	85	76	88	73	68
	28	100	114	108	117	92	84
	90	113	134	115	128	-	98
	260	118	138	119	132	-	-

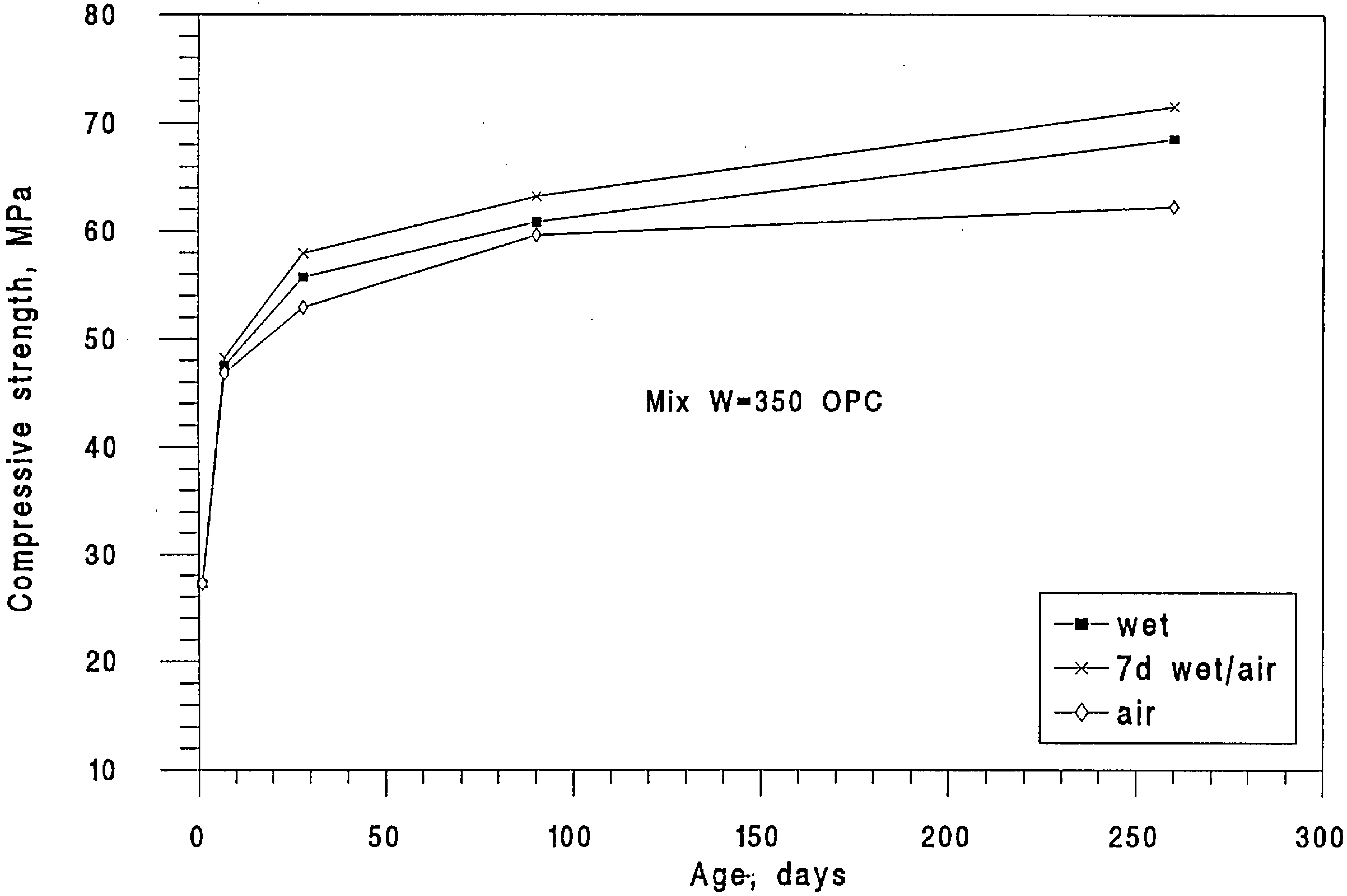


Figure 4.3 Effect of curing on compressive strength for control mix W

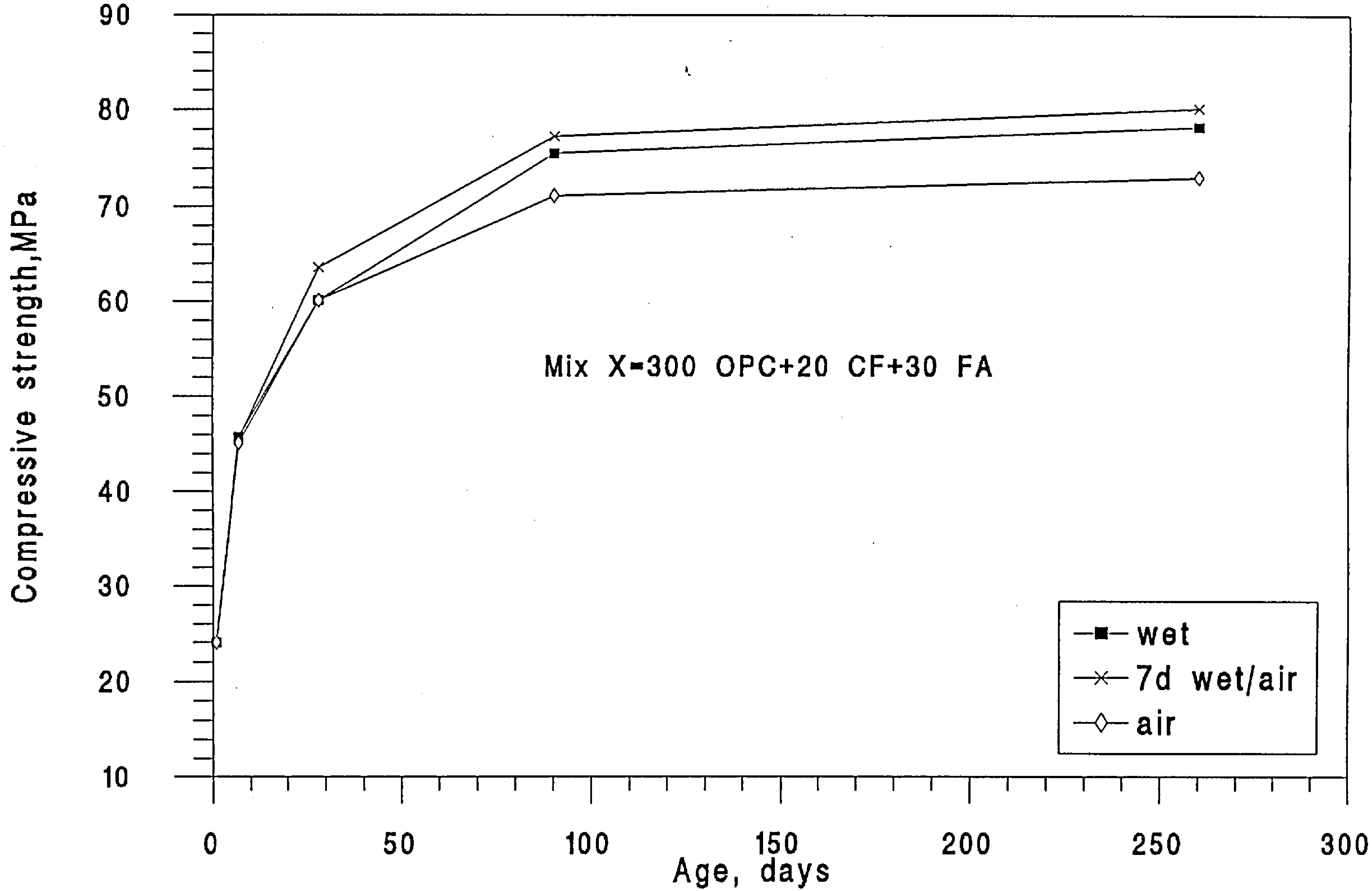


Figure 4.4 Effect of curing on compressive stringth for mix X

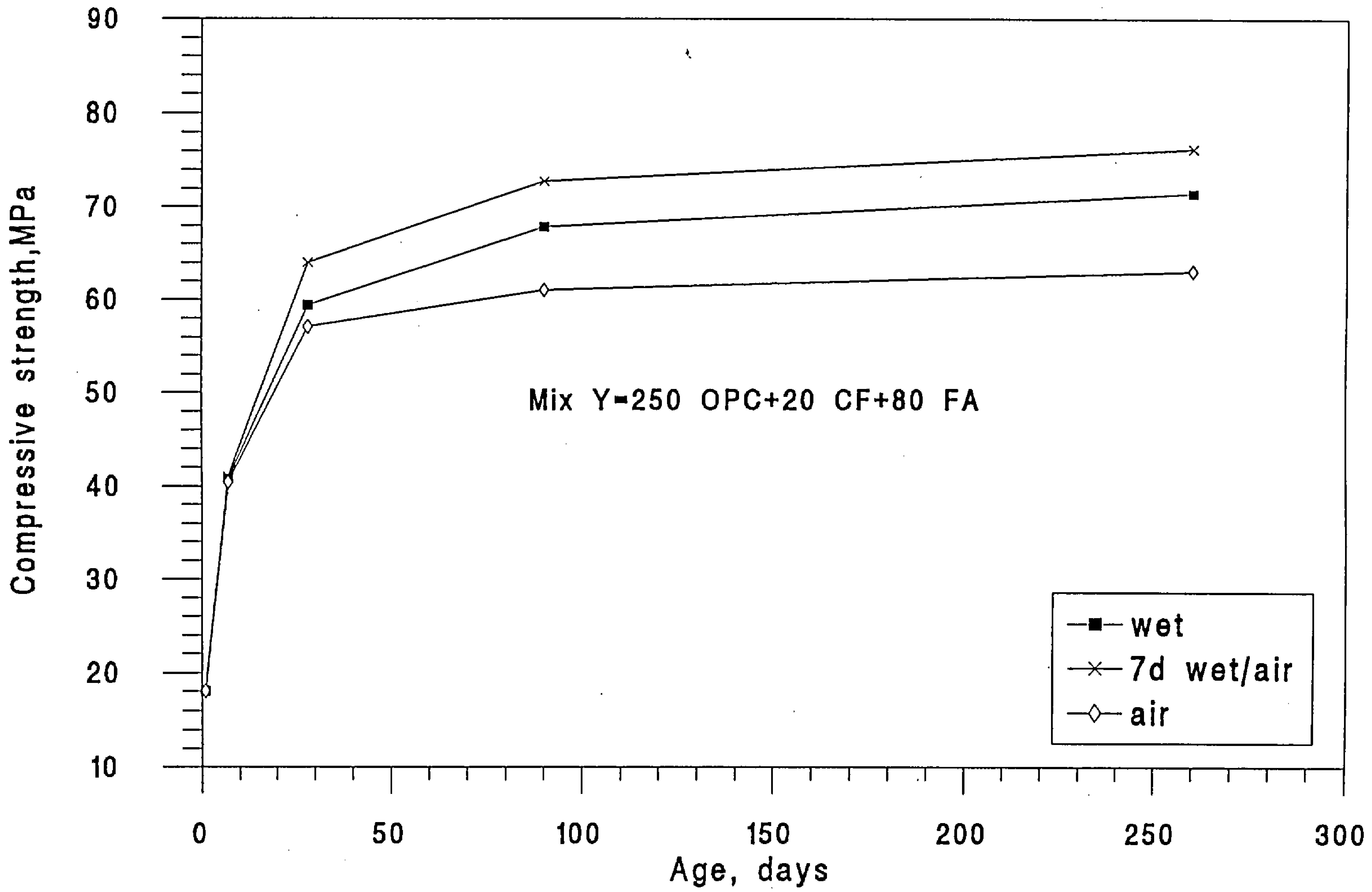


Figure 4.5 Effect of curing on compressive strength for mix Y

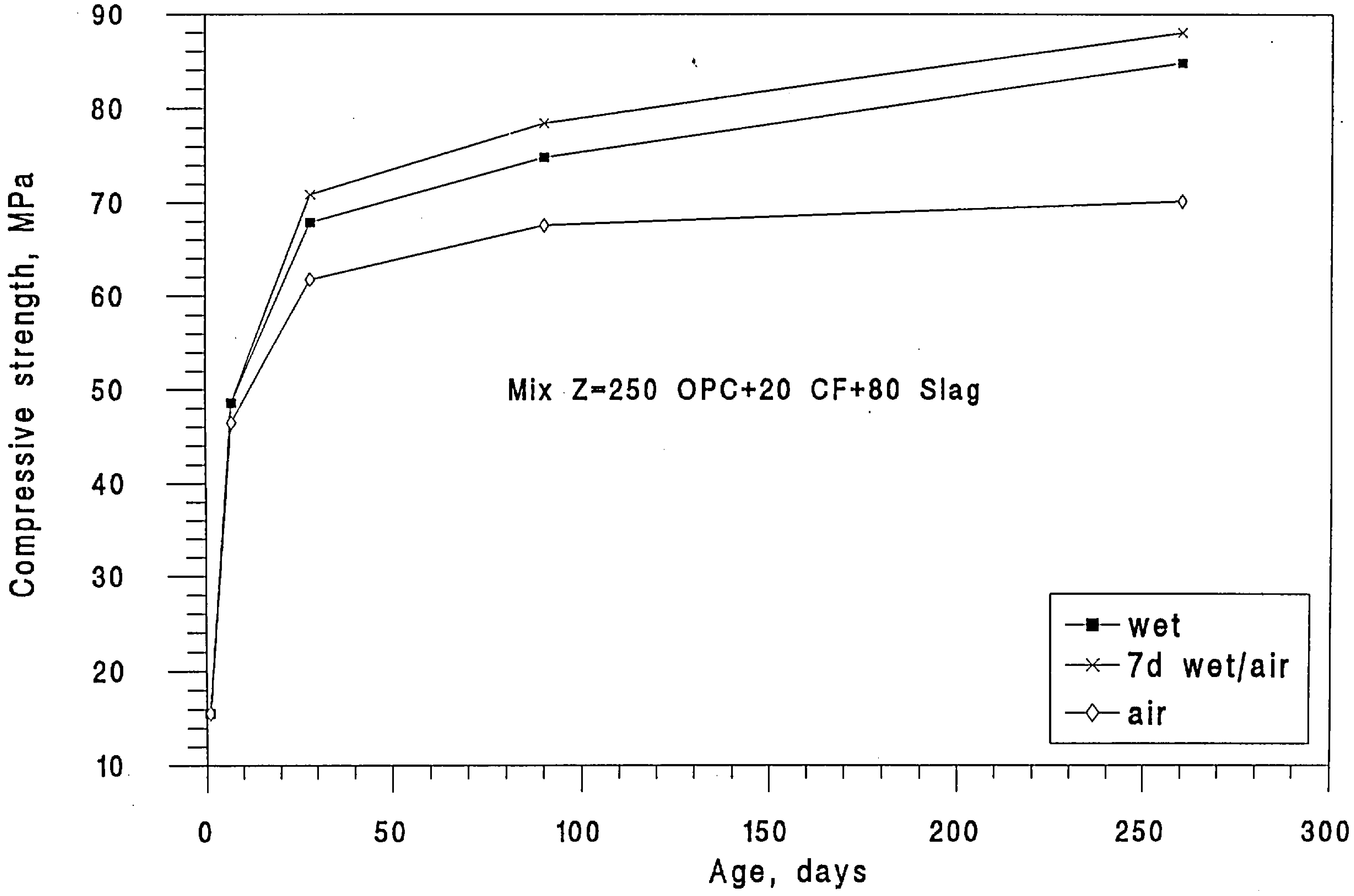


Figure 4.6 Effect of curing on compressive strength for mix Z

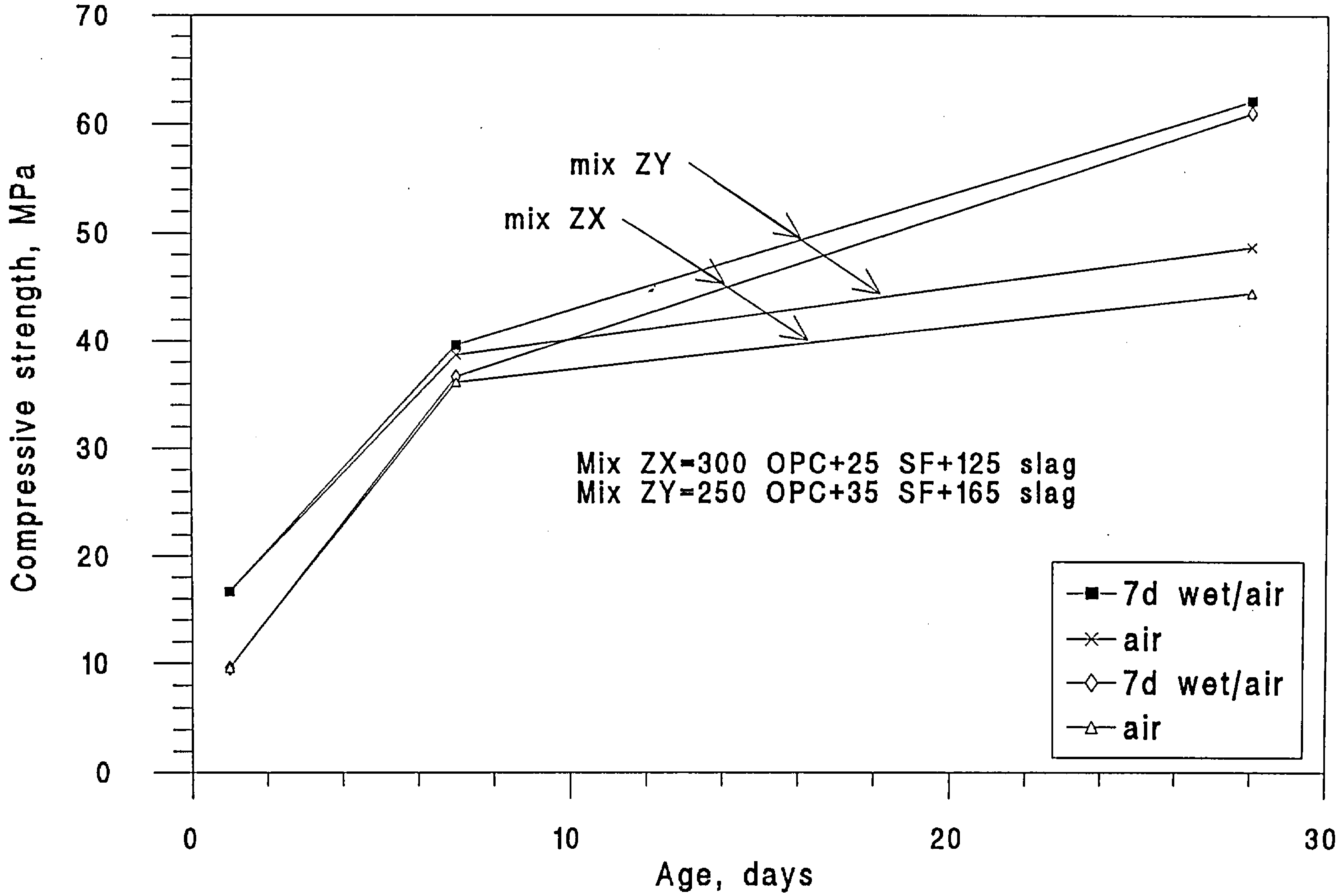


Figure 4.7 Effect of curing on compressive strength for mixes ZX and ZY

concrete sample, and 2) due to increase of compression pressure the pores (holding some water) bursts causing internal microcracing for release of pressure.

The results also show that early age strength development up to 7 days of age were not significantly influenced by the type of curing, whether wet curing or 7d wet/air or air curing was employed, and this was the case with all the cementitious mixes investigated. This is in agreement with other researchers findings [70].

The modified cube strength variations for mix W (control) under wet, 7d wet/air and air curing conditions and at different ages are shown in Fig 4.3. The 7d wet/air- cured specimens at 20°C displayed the highest compressive strength, followed by the water-cured specimens at 20°C, and the air-cured in laboratory at 20°C at all ages of curing. For example at age of curing of 28 days the compressive strength values were 55.7, 57.9 and 52.9 MPa for wet, 7d wet/air- and air-cured specimens at 20°C respectively, but at long term age (260 days), the compressive strength values were 68.5, 71.5 and 62.2 MPa. This indicates that variations between the strength development at the three curing conditions becomes smaller as the age of curing increases. Also it was shown that the rate of increase of strength development between wet and 7d wet/air cured specimens at 90 and 260 days was the same (109 and 124 as a percentage of 28 days strength), whereas this rate for air cured specimens was higher between 28 and 90 days and afterwards slows to reach 118% of its 28 days strength (Table 4.6).

In Figure 4.4 the variation in compressive strength development of concrete mixture X with age under various curing conditions are shown. The figure shows that at 28 days age, the 7 d wet/air cured specimens at 20°C exhibited higher compressive strength, 63.6 MPa, compared with the strength of wet- and air-cured specimens which is equal, 60.1 MPa. In addition the same strength values about 45.5 MPa at age of 7 days were observed for the three curing conditions too. However, in this concrete up to 28 day age the air curing seems not detrimental to strength. This might be attributed to the fact that strengthening influence of SF takes place early [34], and also may be due to the very low amount of FA added and therefore its small influence and contribution. In fact, specimens cured for 7 days exhibited slight increased strength development compared to wet cured ones at the ages of 90 and 260 days, namely 77.3 and 80.1 MPa compared with 75.5 and 78.3 MPa respectively at these two ages. But the rate of strength gain as a percentage of 28 day strength development for the 7d wet/air was lower by 4% at 90 and 260 days compared to wet-cured concrete.

In Figure 4.5, the variation of compressive strength development for mixture Y with age under various curing regimes is presented. This mix is similar to the previous one (X), but with 50 kg/m^3 FA more. Similar patterns were observed for the development of 7d wet/air-cured specimens when compared with wet and air cured specimens; this curing condition gave largest values of compressive strength, 72.7 and 76.2 MPa, at the age of 90 and 260 days, respectively. The continuous water cured specimens yielded values of 67.8 and 71.4 MPa, whilst values of 61 and 63 MPa were obtained for air-cured specimens at the ages of 90 and 260 days respectively for both curing regimens. At these two ages, both 7d wet/air- and wet-cured specimens developed 115 to 120% of their 28 day strength compared to a development of only 50% of this rate (107 to 110%) for air-cured specimens which clearly reflects the adverse effects of no curing at all, and that, as FA amount increases, the concrete is more sensitive to inadequate curing and therefore the significance of the 7d wet/air curing. This point has been emphasised by other researchers as well [39,84].

Figure 4.6 compares the modified compressive strength development of slag/SF mixture for the various curing conditions. At all ages the specimens that were initially water cured for 7 days and then exposed to air curing attained the highest compressive strength, whereas the air cured concrete had the lowest strength values. Between 28 and 260 days 7 d wet/air cured concretes achieved higher strength than the wet cured concrete (70.9 - 88.0 MPa compared with 69.1 - 84.8 MPa), whilst the air-cured concretes showed only 61.7 to 70.1 MPa increase. The 7d wet/air- and wet-cured concretes show the same increasing order of strength about 110 to 125% of their 28 day strength compared with 109 to 114 as a percentage of 28 day strength for air-cured specimens at 90 and 260 days respectively. On the other hand, the difference between both 7d wet/air- and wet-cured concretes and air cured concrete strengths is much greater with slag/SF than FA/SF concrete which means that exposure to a drying internal environment was detrimental to strength development. As a consequence, more attention should be paid on site, specially in hot climates, and a minimum 7 day curing period has to be recommended to realise the strength potential of slag/SF concrete. The same periods of curing were recommended by the others as well [15]. On the other hand, the rate of strength development of air cured concrete was lower than for the 7d wet/air- and wet-cured concrete and the strength approached a value of 71 and 73 MPa at 90 and 260 days showing the disadvantage of non-curing practice on long term strength developments.

The compressive strength developments of both of the slag/SF concrete mixes (ZX and ZY) 7d wet/air- and air-cured at 20°C are shown in Figure 4.7. Only two curing conditions were chosen for these two mixes, because the results obtained under wet curing conditions were somewhat close to that of the 7 day wet/air-cured concrete and followed similar trends. It is evident that compressive strength development of both concretes is more adversely affected by no curing than the 7d wet/air-cured concretes, the effect being more pronounced at higher levels of slag addition in case of ZY mixture at 28 day ages, where compressive strength values of 61 and 44.4 MPa were obtained for ZX and ZY mixes, respectively. As a result it could be stated that curing has to be considered as an essential ingredient of mix design, especially for the most critical period at early curing which is more consistent with general practice. At the same 28 day age, the compressive strength values for 7d wet/air-cured specimens were about the same, 62.1 and 61 MPa for ZX and ZY mixes, respectively. However, allowing both ZX and ZY concretes to develop strength under 7 day wet/air-cured curing conditions will show further development of compressive strength and further gain in durability performance, and the difference in strength at later ages might not be significant; on the other hand, inevitably the rate of strength gain of both air-cured concretes declines and strengths may approach a limiting value, and mix ZY probably might show retrogression of compressive strength.

In summary, the following points could be stated: Barring the ZY mixture under no curing regime, all the concrete mixtures were able to develop the required 28 day strength at 50 MPa under various curing conditions. The early compressive strength and its development for all concretes were not affected by the curing conditions adopted to the age of 7 days, each mix exhibited about the same compressive strength values at age of one and 7 days. It does not mean, however, that there is no significance for curing and that strength can be brought out even without curing, but it might be explained by saying that there was sufficient amounts of moisture in the concrete to continue the hydration to a stage adequate not to impair the strength for the period (1 to 7 days). Differences can be readily seen when concrete mixtures were compared at later ages of curing.

The 7d wet/air-cured concretes exhibited the largest compressive strength compared to wet and air-cured concretes. Whilst the air-cured specimens displayed the lowest compressive strength values in all mixes considered and at all later ages of curing, this was as explained previously likely to be due to poor curing (air) which did not provide an ample quantity of water to the specimens for hydration process to take place.

With the exception of mix X the rate of strength development as a percentage of 28 day strength of the 7d wet/air-cured concretes was similar to wet-cured ones, whereas, as expected, this rate was lower for air-cured concretes.

Finally, early first 7 day curing, the most critical period, is recommended and action has to be taken to ensure its application especially on site. This period must be sufficient for composite cement concrete to develop proper strength and durability.

4.3.4 Effect of Cement Replacement Materials

The results of the compressive strength tests on concrete mixes given in Table 4.2 and shown in the previous section are presented in Figures 4.8 to 4.10 in terms of the effect of cement replacement materials on the compressive strength of concrete.

The results show that the incorporation of SF increased the compressive strength of all concretes under various curing conditions at the age of 28 days and onwards as compared with the compressive strength of the control concrete (350kg/m^3 OPC). The only exception was the concrete mixture ZY cured under air. The rate of strength development was high at early ages and gradually decreased at later ages. The concrete mix Z which incorporated 20 kg/m^3 SF + 80kg/m^3 slag became increasingly stronger relative to the control and other concrete mixes; with increasing time, it exhibited the largest values of compressive strength even at the age of 7 days.

Figure 4.8 demonstrates the compressive strength development for the W, X, Y, and Z concretes water cured for 7 days prior to air curing at 20°C in a laboratory environment with 0.45 water/binder ratio (w/b) and SF content of 20 kg/m^3 with the exception of the control mix (no SF). It can be seen that the strength development pattern of concrete with the mineral admixture at 28 days provides an indication of the cementitious properties and/or pozzolanic activity of the slag and FA at this stage, especially for concretes with lower slag content (20 kg/m^3 SF + 80 kg/m^3 slag) which exhibited the largest compressive strength at all ages of curing followed by both 30 and 80 kg/m^3 FA concretes, while the control concrete showed the lowest strength. For concrete mixture Z incorporation of 20 kg/m^3 SF was sufficient to cause 23% increase in strength compared with the strength of the control concrete, and about an 11% increase in strength compared to both FA/SF concretes. At 90 days the same ranking existed between these concretes, except that the strength of 30 kg/m^3 FA concrete was about the same (77.3 MPa for X concrete vs 78.4 MPa for Z concrete). At later ages more variations were observed in the compressive strength development of these concretes, the plain cement concrete failed to develop as high a compressive strength as its counterparts containing mineral admixtures; it reached 71.5 MPa, while the increased slag/SF (80kg/m^3) concrete exhibited still higher compressive strength of 88 MPa, though the two FA/SF concretes have a lower compressive strength (80.1 and 76.2

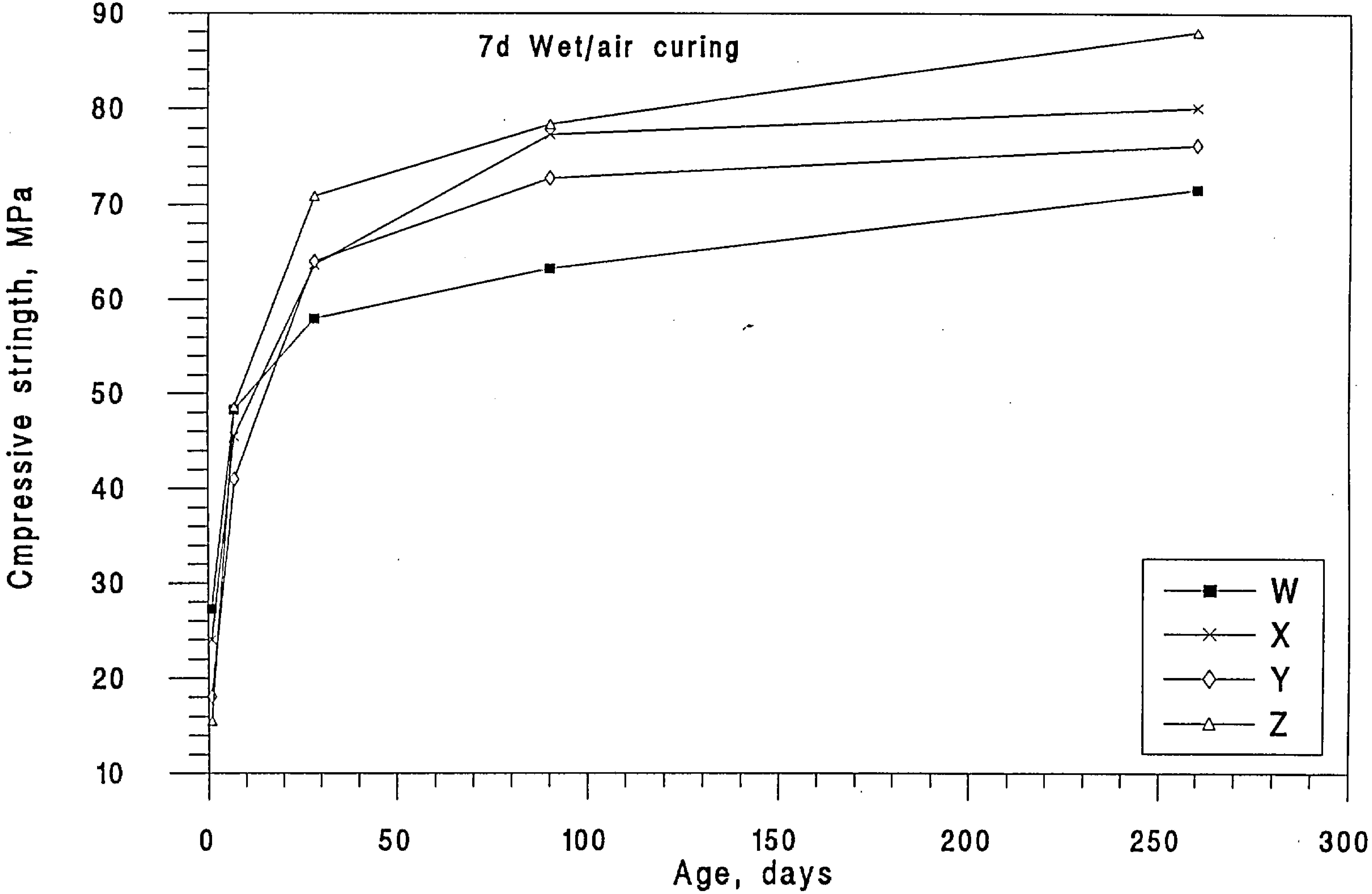


Figure 4.8 Effect of mineral admixtures on compressive strength for mixes W,X,Y,Z and ZY

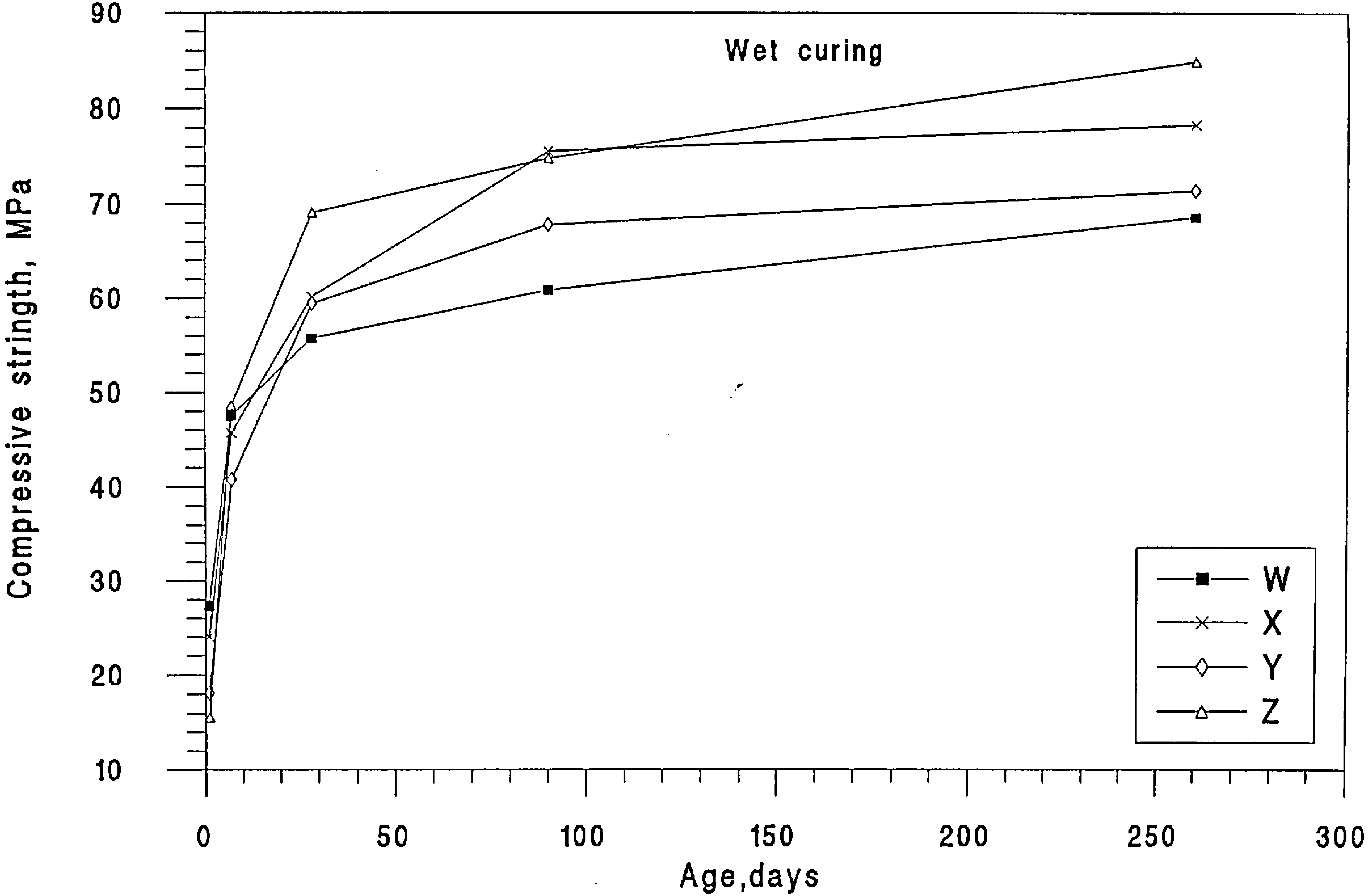


Figure 4.9 Effect of mineral admixtures on compressive stringth for mixes W,X,Y,Z and ZY

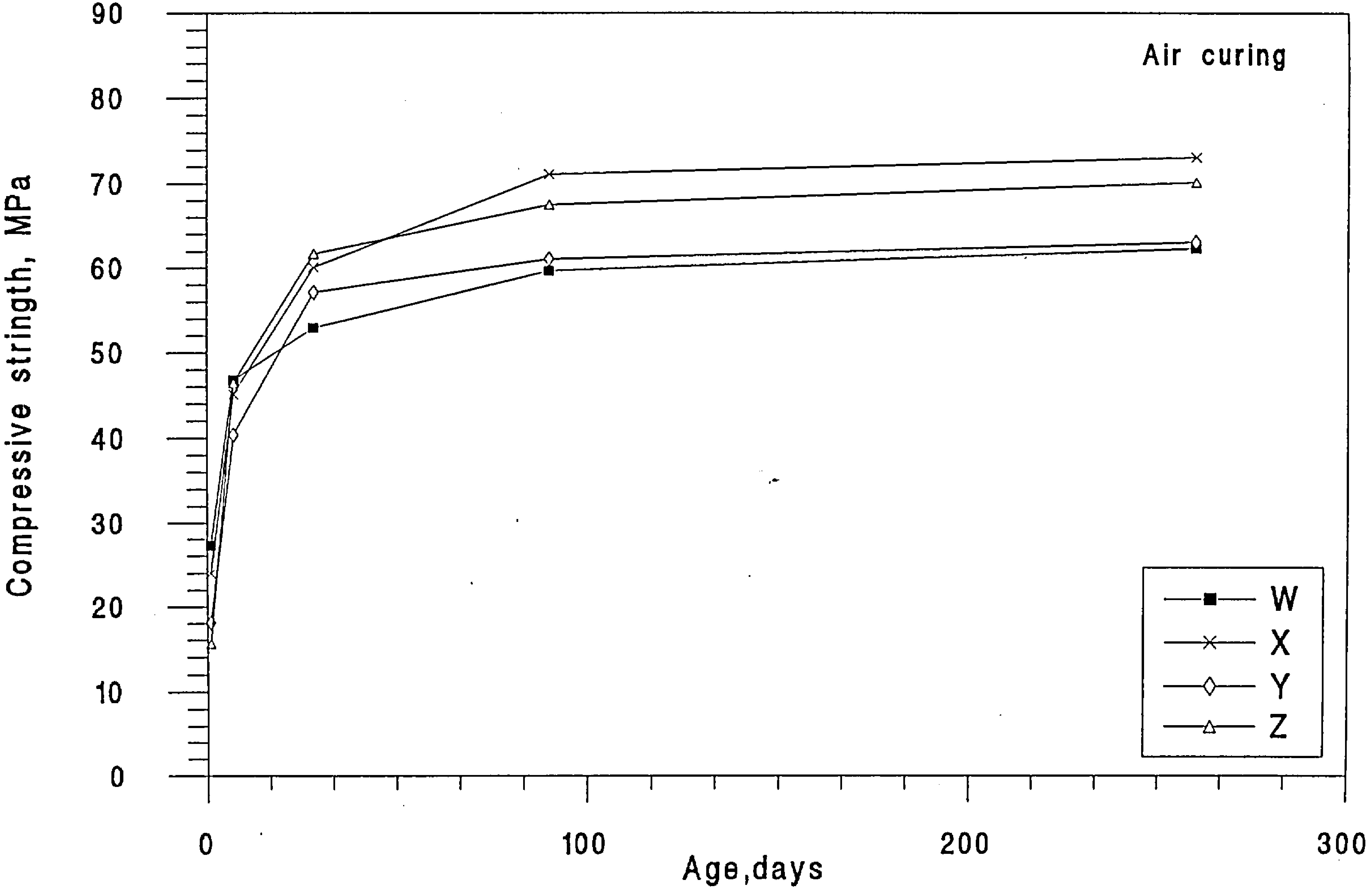


Figure 4.10 Effect of mineral admixtures on compressive stringth for mixes W,X,Y,Z and ZY

MPa) than the Z concrete. However, further increase in the amount of SF and slag did not result in a significant increase in compressive strength, the differences in strength compared to control concrete were small; and the compressive strength of the control approached the values for the ZX and ZY concretes, 62.1 and 61 MPa respectively at the age of 28 days (Figure 4.7). Besides it is noteworthy that with a very slight increase in SF amount (from 25 to 35 kg/m^3) and 40% slag replacement a 50 kg/m^3 of cement was conserved (advantage from economical point of view) and the smaller compressive strength of concrete at the age of 28 days due to slag incorporation was completely overcome. In other words strength development of portland cement/slag concrete was not impaired by the addition of 165 kg/m^3 slag, and 35 kg/m^3 SF was enough to boost the strength of this concrete to a level that was better than that of the control concrete. Therefore it is suggested that addition of 10% SF would enhance the low early-age compressive strength of OPC/slag concrete and makes it possible to produce long-term high strength concrete, provided it is moist cured at least for 7 days. In fact the strength of OPC/slag and OPC/FA concretes steadily increases with the increasing additions of SF to these concretes, but to a certain limit. A similar approach was successfully taken by other researchers.

On the other hand, consider X and Y concretes (Fig. 4.8); for example, at the age of 28 days both concretes exhibited the same compressive strength value of 64 MPa compared to 57.9 and 71 Mpa for control and Z concretes, respectively. But at 90 days as a result of increasing FA amount a reduction in strength for Y concrete was obtained, 75.5 and 67.8 MPa for X and Y mixes, respectively; with further hydration, the difference in strength was observed, strengths of 80.1 and 76.2 MPa were achieved at later ages of 260 days although the gap appears to be narrowing slowly with time. In fact this decrease in strength at a constant water/binder ratio was expected but as FA can improve the workability of concrete it is possible to reduce water in the mix design which leads to higher compressive strength for this reason, and also as workability is an important factor for the concrete in practice, the mixes were prepared at constant workability with the use of superplasticizer. For 20 kg/m^3 (about 6%) SF addition the strength gains at later ages for 80 kg/m^3 FA content were somewhat marginal compared to control concrete; however, when substantial increases could be achieved with increasing amounts of the SF besides FA, 30% FA and 8% SF by weight of cement replacement is suggested. Similar concrete with water/(cement+FA) ratio of 0.6 and incorporation 10 and 20% silica fume increased the strength by 32 and 55% respectively compared to only OPC concrete [44].

Modified compressive strength development for mixes W,X,Y and Z continuously cured in water at 20°C is demonstrated in Figure 4.9. The water/binder ratio and SF content were constant, 0.45 and 20 kg/m^3 respectively. The figure shows an almost similar trend to that in Figure 4.8 and shows that under continuously water curing all concretes steadily developed strength with age, reaching their target strength of 50MPa at 28 days.

At 28 days, both FA/SF concretes yielded similar values of compressive strength and registered an increase of about 8% over the control concrete strength, while for the slag/SF concrete the corresponding increase in strength was 22%. As would be expected the mixture with 80kg/m^3 slag always showed higher strength than concrete with FA/SF is due to the slag admixtures containing more reactive glass[87], when the hydration of slag started, it produced more and denser hydrated products after full hydration of slag component in the concrete[1]. At the age of 90 days, the compressive strength values were 60.8, 75.5, 67.8 and 74.8 MPa for mixes W,X,Y and Z, respectively. The 30kg/m^3 FA concrete showed slightly higher value then mix Z. Between 28 and 90 days there is a tendency for 30kg/m^3 FA concrete to develop strength at a higher rate than the control and slag/SF, which was 126% of the 28 day strength compared to about 110% for the control and slag/SF concretes. But in general the results indicate that FA/SF concrete strength decreases with increasing FA content and as the duration of the curing period increases the differences in the rate of strength development between concretes becomes smaller, the range is shown in Table 4.6. However, the absolute strength was still highest for the slag/SF concrete, 84.8 MPa at the age of 260 days, compared to 68.5, 78.3 and 71.4 MPa for mixes W, X and Y respectively, such higher increment in strength at later ages in concrete containing slag and silica fume compared to control concrete indicates the benefits of slag incorporation besides silica fume.

The modified comprehensive strength development for all concrete mixes cured in air at 20° (Lab environment) on demoulding at 24 hour is shown in Figure 4.10 and their data are illustrated in Table 4.5. These data emphasise the need for early water curing for a minimum period of 7 days for all concretes and in particular for the slag/SF concretes. It can be clearly seen that strength development of 125 and 165 kg/m^3 slag concretes is more adversely affected by no curing compared to the control and other concretes. Concrete with 165 kg/m^3 slag failed to reach its target strength at 28 days, whereas concrete with 125 kg/m3 slag almost reached its target strength at this age. This is not unusual for concrete incorporating that much amount of slag which is more cementitious and less pozzolanic almost like OPC and allowing the concrete to dry effectively stops the further development of strength and further gain in durability performance which is obviously apparent under adequate water curing where sufficient water is available for full hydration. Also the data show that their is probably a limiting amount of slag beyond which, without further curing, strength may not fully develop. On the other hand the 28 day strength of X and Y concretes was about 15 and 10% respectively higher than the control concrete strength. The strength of mix X was 5% higher than of that mix Y, and with aging this difference in strength increases in favour of mix X, indicating that effect of air curing could be more adverse on high FA replaced concrete. The 28 day compressive strength of control concrete was slightly higher than the target strength, and reached a value of 52.9 MPa compared with higher, but closer, strength value of 60.1, 57.1 and 61.7 MPa for mixes X, Y and Z, respectively.

At 90 days age, mixture Y with 80 kg/m^3 FA showed a modest improvement and registered a strength value of 61 MPa close to that of control strength, 59.6 MPa. Beyond this age, mixture continued to show slightly hydration and followed the same pattern as the strength development of control concrete with small differences in strength to give 62.2 and 63 MPa for control and Y mixes, respectively. On the other hand, revese to its trend under wet and 7d wet/air curing conditions the 80 kg/m^3 FA mixture has shown a better performance than 80 kg/m^3 slag. At the age of 90 and 260 days, slag concrete has shown 5% lower values for compressive strength, 67.5 and 70.1 MPa, while for FA concrete it was 71.1 and 73.2 MPa respectively at these ages. Its strength development as a percentage of 28 day strength was also 12% slower than that of FA concrete at these ages.

This reduction in the compressive strength and rate of strength gain in slag concretes compared to FA and control concretes under air curing is expected; and it could be said that strength of concretes containing slag/SF are more vulnerable to no curing than either plain OPC or FA/SF concretes. Swamy [19], stated that no curing after demoulding under internal lab environment seems to have had an adverse effect on strength increase in mixtures at 50 and 65% slag replacement level and it may show some strength retrogression. However, with concrete containing FA which contributes to strength through pozzolanic reaction, the strength development is also susceptible to poor or inadequate conditions of curing than concrete containing Portland cement alone. As a consequence, more attention should be paid on site to achieving the specified curing periods.

Further the figure shows that both 80kg/m^3 FA and slag concretes develop about 20 and 15% respectively higher compressive strength than the control concrete beyond the age of 28 days. At the age of 90 days, the compressive strength values were 59.6, 71.1 and 67.5 MPa for mixes W, X and Z; and at the age of 260 days the corresponding values were 62.2, 73 and 70.1 MPa. It appears also from data that the three concretes registered an equal increase of about 5% over their 90 day strength indicating the bad effect of no curing and very slow hydration.

4.3.5 Comparison with Cube Compressive Strength

The compressive strength of wet-cured specimens for mixes W, X, Y and Z tested by the modified cubes method and the cube method for the ages 1, 7 and 28 days was aralyized.

The findings were as follows:

1. The results show that all mixtures were able to develop the required 28-day cube compressive strength of 50 MPa, and that concrete containing combination of SF or slag and SF can be designed to give consistent 28 day strength results.

2. Strength obtained using modified cube method was slightly higher than the cube method, this slight increase in modified cube strength is due to the confined effect [31]. The results are also approximately in agreement with BS1881:1952 which assumes the strength of the modified cube to be on the average 5% higher than that of a cast cube of the same size.

3. The results confirm that the loss in early-age-compressive strength due to the partial replacement of cement by either FA or slag could be overcome by a given addition of SF.

4.4 Flexural Strength

4.4.1 Effect of Curing

The results obtained indicate that air-cured specimens under a laboratory environment yielded the lowest values of flexural strength in all concrete mixes. The influence of various curing conditions on the flexural strength of different concrete mixes is shown in Tables 4.7 & 4.8 and Figures 4.11 to 4.15.

Figure 4.11 shows flexural strength development of mix W; the 7d wet/air-cured specimens displayed the highest strength values at most ages. At 7 days both wet and 7d wet/air cured specimens showed close strength values, 5.6 and 5.82 MPa respectively, as well as at the age of 28 days, 6.1 and 5.82 MPa. Whereas for air-cured specimens about

Table 4.7 Results of flexural strength of all mixes under various curing conditions

Mix type, kg/m^3	Curing Age,day	Flexural strength, MPa			Percentage of 28 day strength, %		
		wet	7d wet / air	air	wet	7d wet /air	air
350 OPC	1	3.73	3.73	3.73	61	64	82
(W)	7	5.60	5.80	3.98	92	100	87
	28	6.10	5.82	4.56	100	100	100
	90	6.16	6.84	6.22	101	118	136
	260	6.00	6.64	5.80	98	114	127
300 OPC	1	3.75	3.75	3.75	50	59	72
+20 SF	7	5.44	5.32	4.74	73	84	90
+30 FA	28	7.42	6.30	5.24	100	100	100
(X)	90	7.30	7.78	7.00	98	123	134
	260	6.8	6.9	6.20	92	110	118
250 OPC	1	3.28	3.28	3.28	61	53	62
+20 SF	7	4.64	4.66	4.28	86	75	81
+80 FA	28	5.42	6.18	5.26	100	100	100
(Y)	90	6.74	6.86	6.04	124	111	115
	260	6.56	6.30	5.30	121	102	100
250 OPC	1	2.97	2.97	2.97	49	52	55
+20 SF	7	5.36	5.08	4.34	89	88	81
+80 Slag	28	6.02	5.76	5.36	100	100	100
(Z)	90	8.50	8.32	8.02	141	144	150
	260	6.88	6.14	5.08	114	107	95
300 OPC	1	-	3.31	3.31	-	58	71
+25 SF	7	-	4.94	3.72	-	86	80
+125 Slag	28	-	5.74	4.66	-	100	100
(ZX)							
250 OPC	1	2.36	2.36	2.36	28	42	58
+35 SF	7	5.24	5.24	3.62	62	92	88
+165 Slag	28	8.48	5.68	4.10	100	100	100
(ZY)	120	7.32	-	4.56	86	-	111

Table 4.8 Flexural strength proporties of silica fume/fly ash and silica fume/slag concrete

Mix type	Curing Age, day	Flexural strength, MPa			Percentage of 28d strength			Flexural strength / compressive strength, %		
		wet	7dwet / air	air	wet	7dwet / air	air	wet	7dwet /air	air
W	1	3.73	3.73	3.73	61	64	82	14	14	14
X	1	3.75	3.75	3.75	50	59	72	16	16	16
Y	1	3.28	3.28	3.28	61	53	62	18	18	18
Z	1	2.97	2.97	2.97	49	52	55	19	19	19
ZX	1	-	3.31	3.31	-	58	71	-	20	20
ZY	1	2.36	2.36	2.36	28	42	58	25	25	25
W	7	5.60	5.80	3.98	92	100	87	12	12	9
X	7	5.44	5.32	4.74	73	84	90	12	12	10
Y	7	4.64	4.66	4.28	86	75	81	11	11	11
Z	7	5.36	5.08	4.34	89	88	81	11	10	9
ZX	7	-	4.94	3.72	-	86	80	-	12	10
ZY	7	5.24	5.24	3.62	62	92	88	14	14	10
W	28	6.10	5.82	4.56	100	100	100	11	10	9
X	28	7.42	6.30	5.24	100	100	100	12	10	9
Y	28	5.42	6.18	5.26	100	100	100	9	10	9
Z	28	6.02	5.76	5.36	100	100	100	9	8	9
ZX	28	-	5.74	4.66	-	100	100	-	9	10
ZY	28	8.48	5.68	4.10	100	100	100	14	9	9
W	90	6.16	6.84	6.22	101	118	136	10	11	10
X	90	7.30	7.78	7.00	98	123	134	10	10	10
Y	90	6.74	6.86	6.04	124	111	115	10	9	10
Z	90	8.50	8.32	8.02	141	144	150	11	11	12
ZY	120	7.32	-	4.56	86	-	111	10	-	9
W	260	6.00	6.64	5.80	98	114	127	9	9	9
X	260	6.80	6.90	6.20	92	110	118	9	9	9
Y	260	6.56	6.30	5.30	121	102	100	9	8	8
Z	260	6.88	6.14	5.08	114	102	95	8	7	7

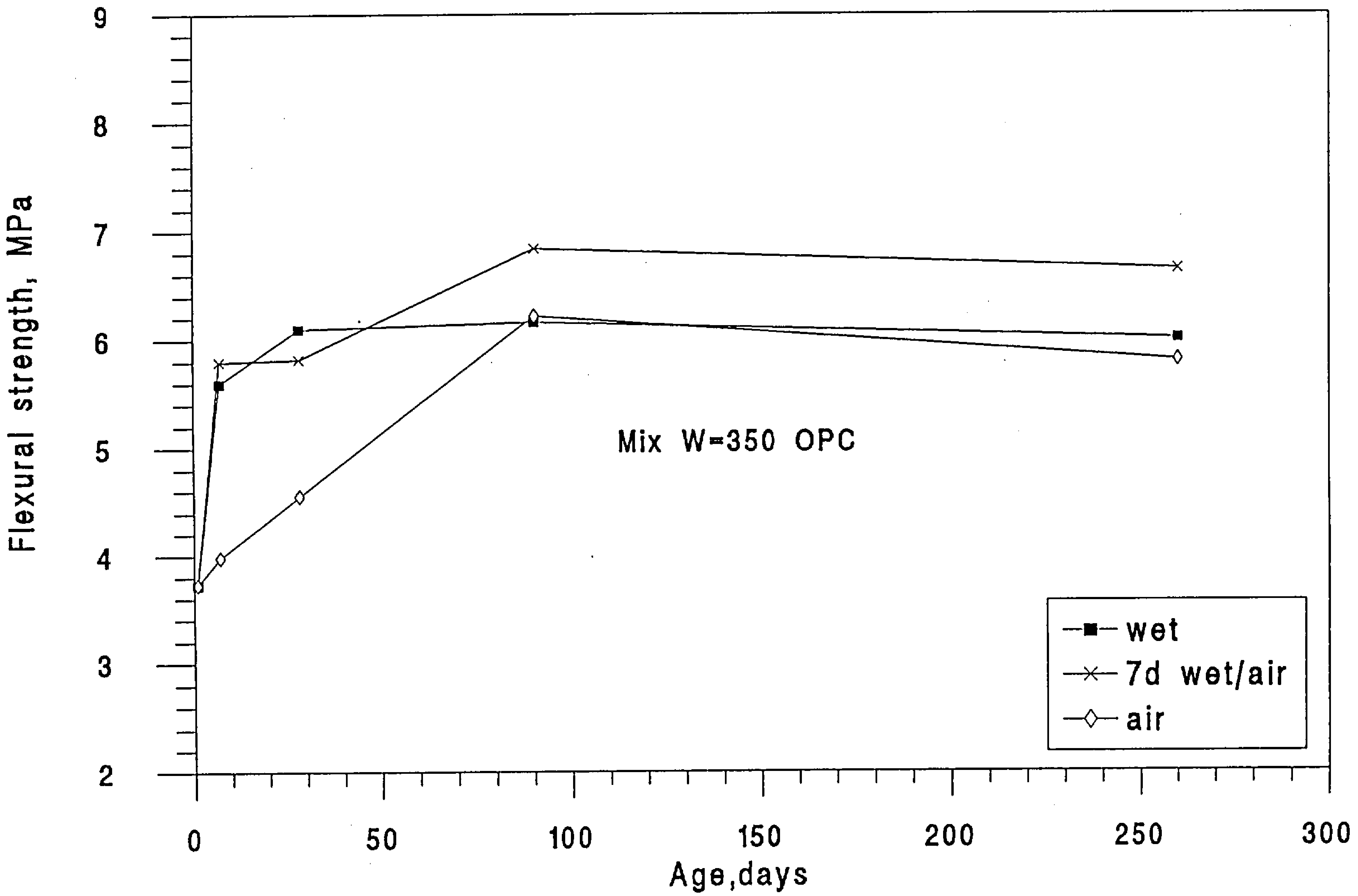


Figure 4.11 Effect of curing on flexural strength for control mix W

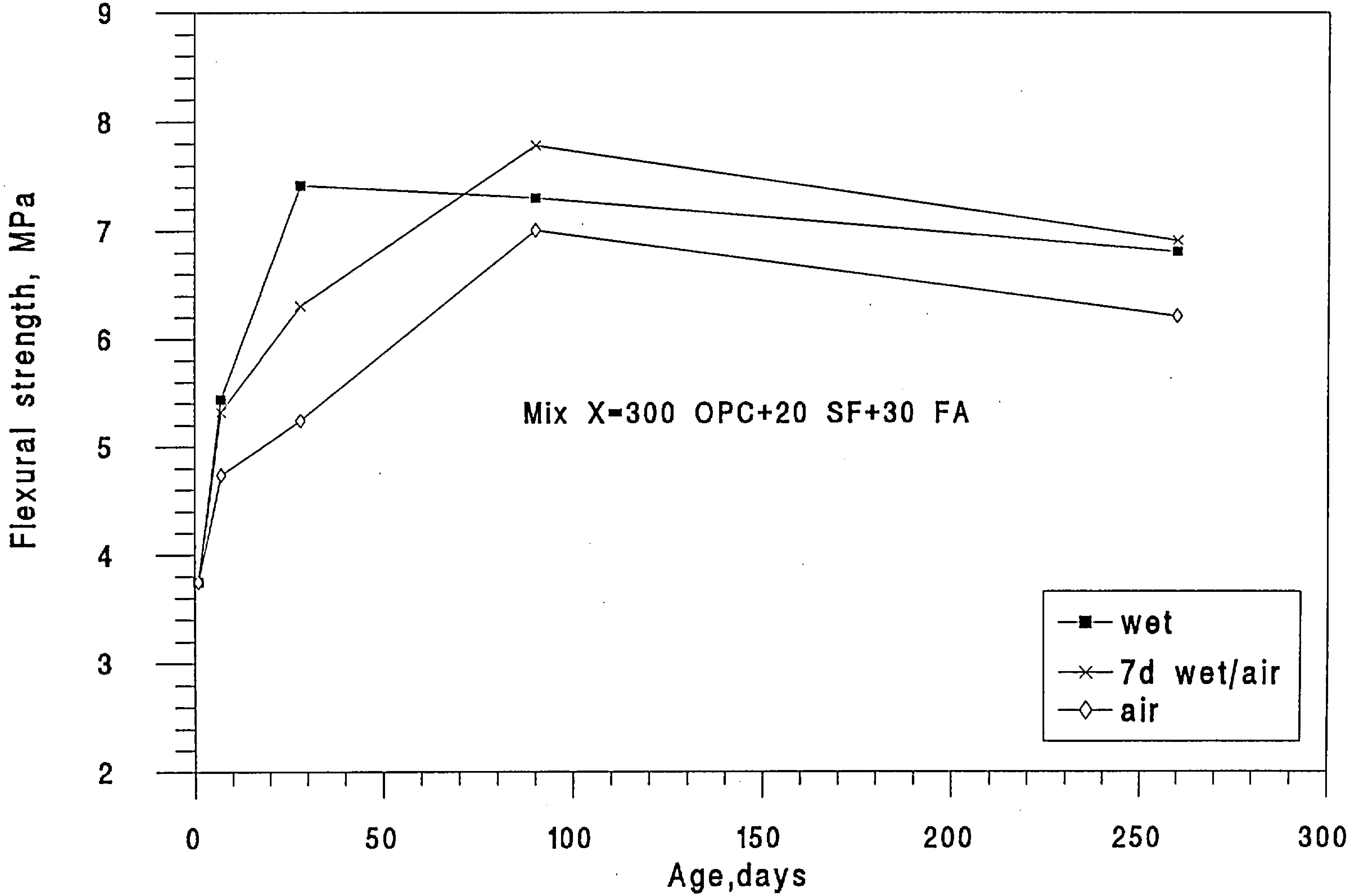


Figure 4.12 Effect of curing on flexural strength for mix X

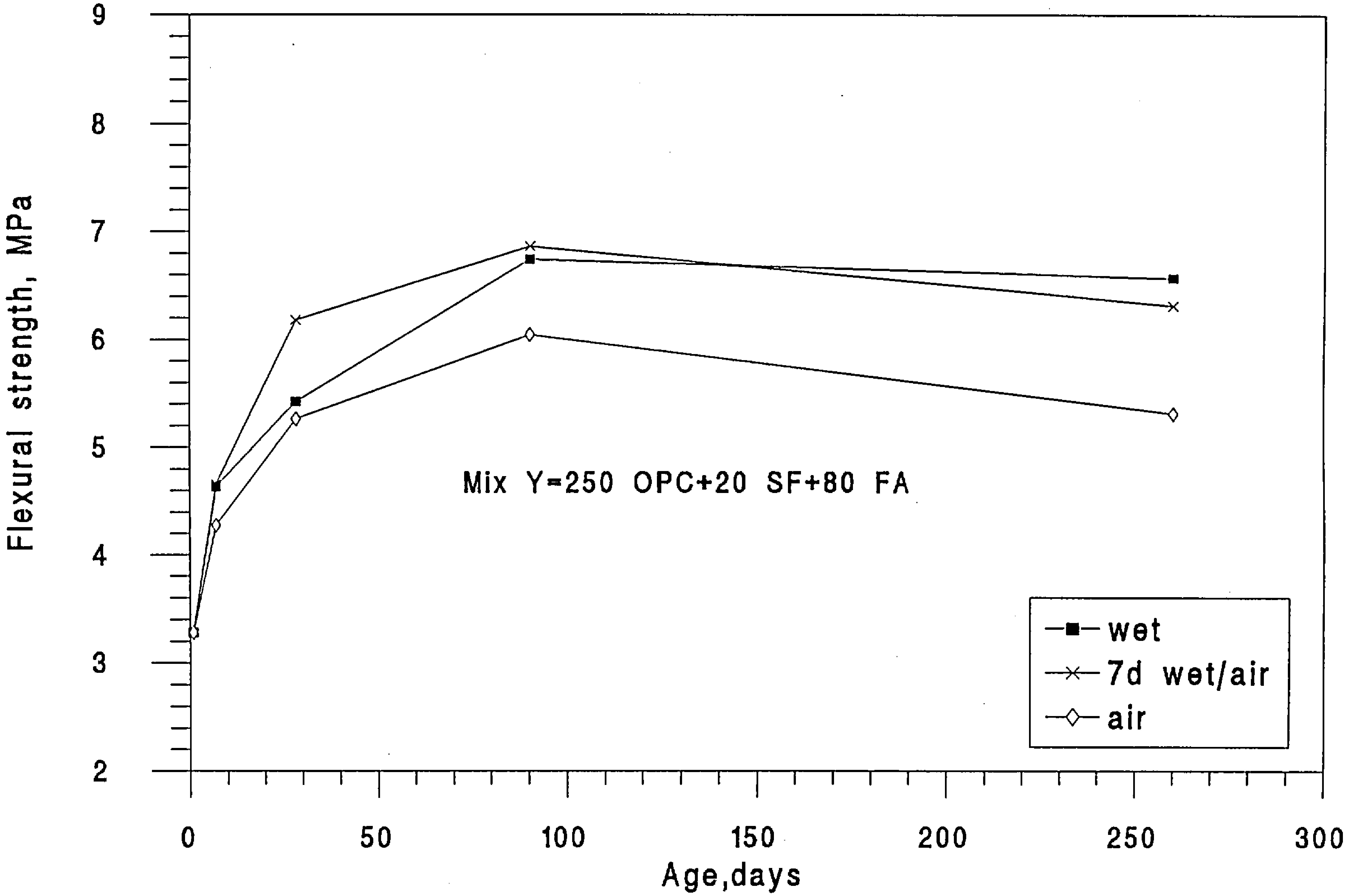


Figure 4.13 Effect of curing on flexural strength for mix Y

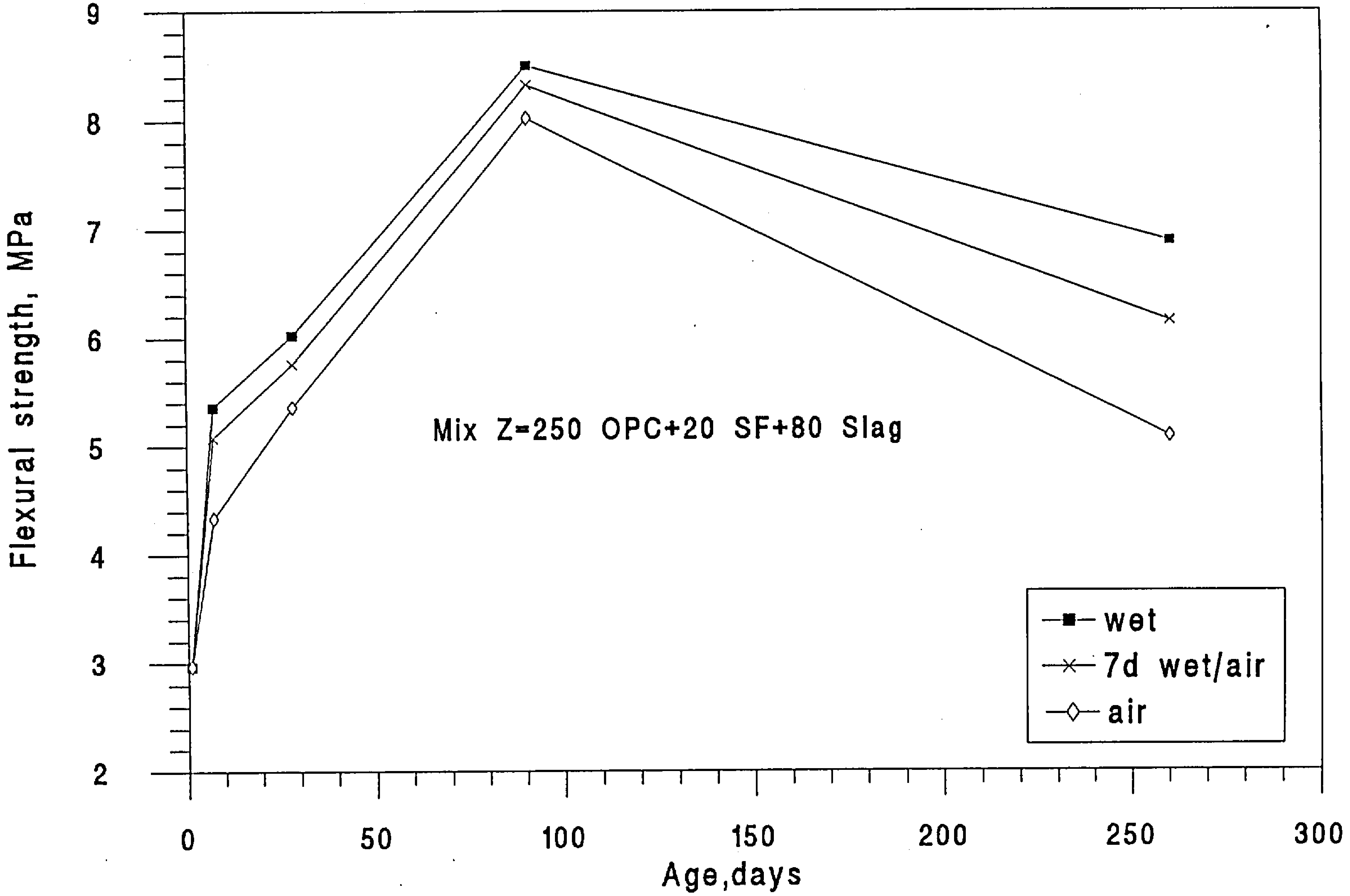


Figure 4.14 Effect of curing on flexural strength for mix Z

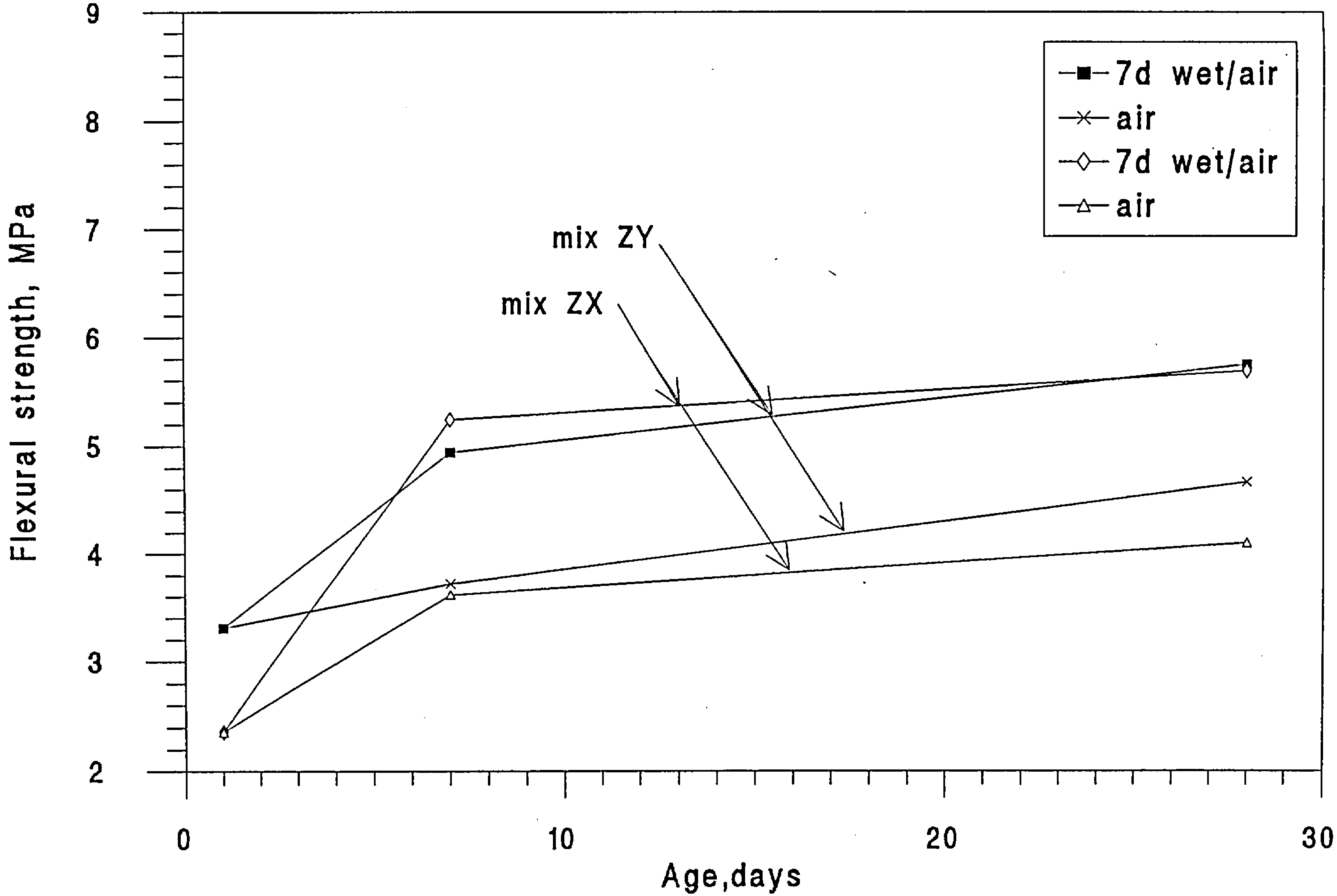


Figure 4.15 Effect of curing and mineral admixtures on flexural strength for ZX and ZY mixes

25% lower strength values were obtained at the same ages, 3.98 and 4.56 MPa, showing the early effect of bad curing. At later ages, it was reversed, 6.2 MPa flexural strength value for both wet-and dry-cured specimens at 90 day age, and a close strength values of 6 and 5.8MPa at 260 days, compared with 6.84 and 6.64MPa for 7d wet/air-cured specimens were obtained at these ages. Also from the data it can be seen that under wet curing no increase in strength was observed beyond the age of 28 days and the strength development was stopped whereas under 7d wet/air- and air-curing still hydration took place and the strength development as percentage of 28 day for air-cured specimens was higher than 7 d wet/air-cured specimens.

The flexural strength development of concrete mixture X under the three curing conditions is illustrated in Figure 4.12. It shows that the flexural strength for wet-cured specimens increased sharply up to 28 days age and then gently decreases afterwards to give a strength value of 7.3 and 6.8 MPa at 90 and 260 days, respectively. For 7d wet/air- and air-cured specimens the strength development started to decrease after 90 days to end up with a value of 6.9 (very close to value to wet cured specimens) and 6.2 MPa, respectively, at age of 290 days. About 10% reduction in strength development as a percentage of 28 day strength at 290 days was observed for wet-cured specimens compared to 110 and 118% development of 28 day strength.

Returning to the age of 28 days, the differences in strength due to the three curing conditions were considerable and values of 7.42, 6.3 and 5.24 MPa were registered under wet, 7d wet/air and air curing conditions, respectively, but at 7 day age the strength value of wet and 7 day wet/air cured specimens were almost the same, 5.44 and 5.32 MPa compared to that of 4.74 MPa for air-cured specimens.

Development of flexural strength for concrete mixture Y under various curing conditions is shown in Figure 4.13. As in Figure 4.12, the 7d wet/air-cured specimens gave the largest flexural strength values up to age of 90 days, followed by wet-and air-cured specimens respectively up to this age. The adverse effect of no curing on strength development can be readily seen. At the age of 7 days, both wet-and 7d wet/air-cured specimens showed about the same strength values, 4.64 and 4.66 MPa, compared with 4.28 MPa for air-cured ones. At the age of 28 days, the 7d wet/air- cured specimens yielded a strength value of 6.18 MPa whereas values of 5.42 and 5.26 MPa were obtained for wet- and air-cured specimens, respectively. At the age of 90 days, the 7d wet/air-cured specimens exhibited the largest strength value of 6.86 MPa same as that of wet-cured ones, 6.74 MPa, which registered the highest strength development rate

(124% vs 111% of the 28 day strength), while the air cured specimens registered about a 10% lower strength value of 6.04 Mpa (Table 4.7).

Beyond 90 days, all specimens showed a reduction in strength. The rate of flexural strength decreasing for wet-cured specimens was slow compared to that of 7d wet/air- and air-cured ones and gave a value of 6.56 MPa compared with 6.3 and 5.3 MPa (102 and 100% of their 28 day strength) for 7d wet/air- and air-cured specimens, respectively. In other words, the flexural strength development between 28 and 260 days was not influenced by the 7d wet/air- and air-curing regimes and their relative effect or strength retrogression was equal or the same.

The results of flexural strength for slag/SF concretes cured under various curing regimens are given in Table 4.7. The strength development for mixture Z is shown in Figure 4.14. Consistently, the wet-cured specimens displayed the highest flexural strength followed by 7 d wet/air- and air-cured specimens respectively, the trend of strength development was similar under the three curing conditions. The flexural strength values at the age of 7 days were 5.36, 5.08 and 4.34 MPa (80-90% of their 28 day strength) for the wet, 7d wet/air- and air-cured specimens respectively, and at the age of 28 days the strength values were 6.02, 5.76 and 5.36 MPa. At 90 days, mixture Z cured under the three curing conditions registered an increase of 40-50% over their 28 day strength and the strength values were 8.5, 8.32 and 8.02MPa for wet-, 7d wet/air- and air cured specimens respectively. Beyond this age, the flexural strength decrease for all specimens was somewhat steep. It is accepted that with increase in age strength retrogression in slag concretes takes place, and it could be detected by pulse velocity and/or dynamic modulus of elasticity testes, however, this high retrogression was not observed by pulse velocity and dynamic modulus of elasticity testes carried out on the specimens used for rupture test. This high reduction in strength could be due to some mechanical problem in testing machine which was reflected on results. Air-cured specimens were more sensitive and showed higher strength loss compared with 7d wet/air- and wet-cured ones, the rate of strength reduction was 95, 107 and 114% of their 28 day strength for air, 7d wet/air and wet cured specimens respectively, at 260 day; and their corresponding strength values were 5.08, 6.14 and 6.88 MPa.

On the other hand, the effect of 7d wet/air- and air-cured conditions on the flexural strength development for concrete mixture ZX and ZY display a different trend as shown in Figure 4.15. It can be seen that 7d wet/air cured specimen produced a higher level of flexural strength for both concretes than that of the air-cured ones, but their strength development as a percentage of 28 days strength was close about 80-90% for both mixes at the two curing conditions.

In general the adverse effect of air curing on flexural strength development in all mixes was readily seen. where these specimens displayed the lowest strength values compared with the other two curing conditions. Further, under 7d wet/air- and air-curing conditions all specimens indicated strength loss after about 90 days, presumably due to non-uniform moisture distribution and the shrinkage cracks. On the other hand the wet-cured specimens continued to develop flexural strength up to 90 days, some loss in strength of some mixes was observed thereafter, but however, the specimens absolute strength values were about the same or higher than their 28 days strength. Despite investigation no explanation was found for these fluctuations, it could be due to some mistake while testing. However the 80 kg/m^3 slag mix exhibited the largest flexural strength values at 90 days under the three curing conditions as will as the strength development rate.

4.4.2 Effect of Cement Replacement Materials

The effect of incorporating mineral admixtures and age on the flexural strength cured in the three curing conditions is shown in Table 4.8 and displayed in Figures 4.16 to 4.20. The table also shows the development of strength as a percentage of 28 day strength and the relationship between flexural strength and compressive strength.

Figure 4.16 shows the flexural strength development for mixes W, X, Y and Z continuously cured under water at 20°C up to testing age. The same amount of SF was added to each mix, 20 kg/m^3 (except for mix W), and the cementitious content was the same, 350 kg/m^3. Under wet curing the flexural strength of all concretes continued to increase up to age of 90 day except mix X which started to decrease slightly after 28 days. At early ages, 1 day, the flexural strength of mixes W and X was about same, 3.73 and 3.75 MPa compared with 3.28 and 2.97MPa for Y and Z mixes respectively. At 7 days the slag/SF specimens strength approaches close to that of the control and 30 kg/m3 FA mixes obtaining a value of 5.36 MPa (90% of 28 day strength) compared to 5.6, 5.44 and 4.64mm^2 for W, X and Y mixes respectively, but still the strength of control concrete was higher. A similar situation was found by carrette [44], that 7 day strength of concrete prisms incorporating FA and SF was lower than the strength of control concrete, a strength value of 5 MPa for 70% OPC and 5% SF and 30% FA was obtained and a value of 5.4 MPa with 10% SF. He found also that the effect of the incorporation of the SF on flexural strength of concrete was less marked than on the compressive strength. These trends at 1 and 7 days were about the same as those observed at 1 and 7 days for the compressive strength in the previous section. The figure shows gradual increase in flexural strength of slag concrete with increasing age. At 28

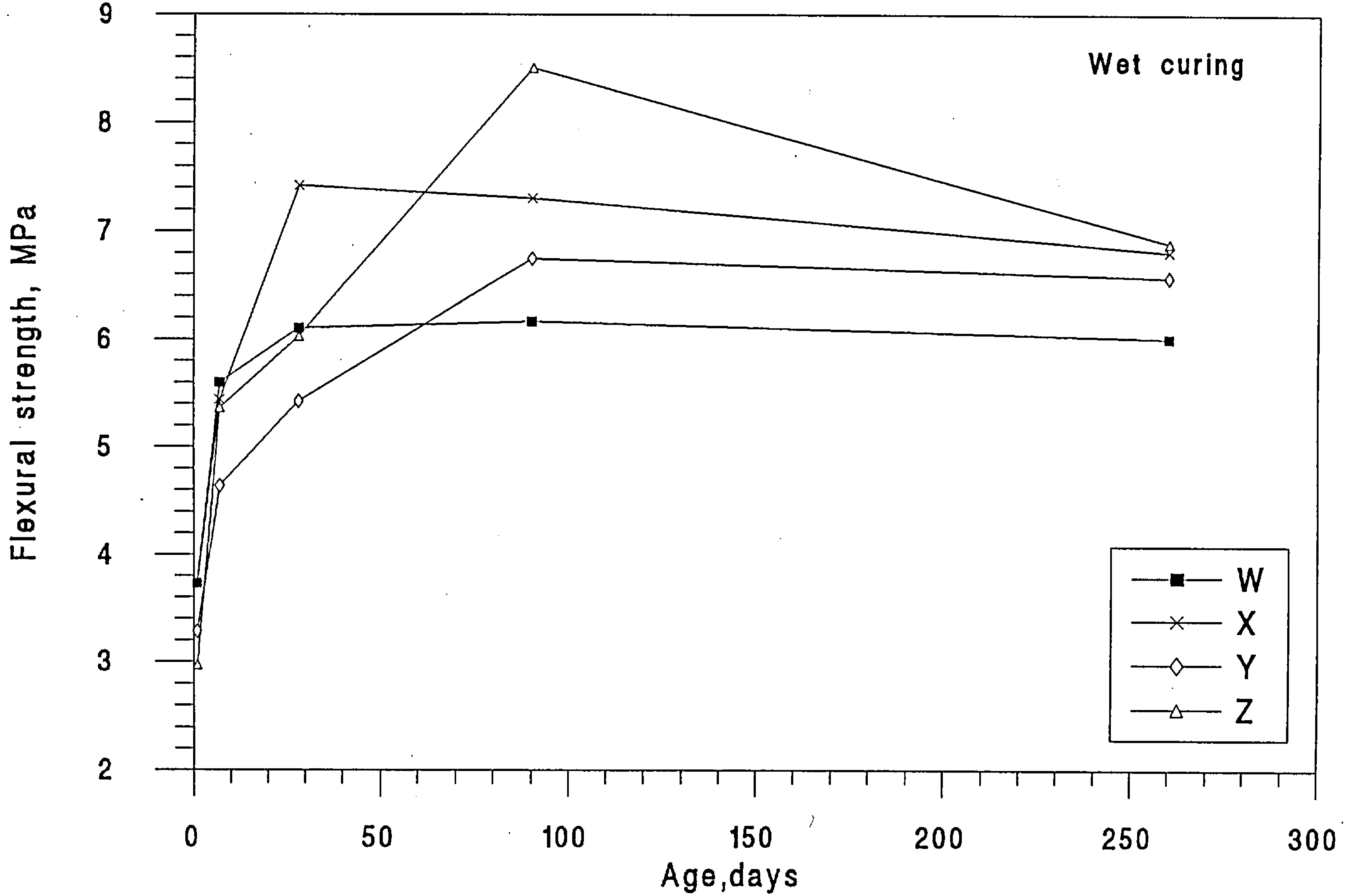


Figure 4.16 Effect of mineral admixtures on flexural strength for mixes W,X,Y,Z and ZY

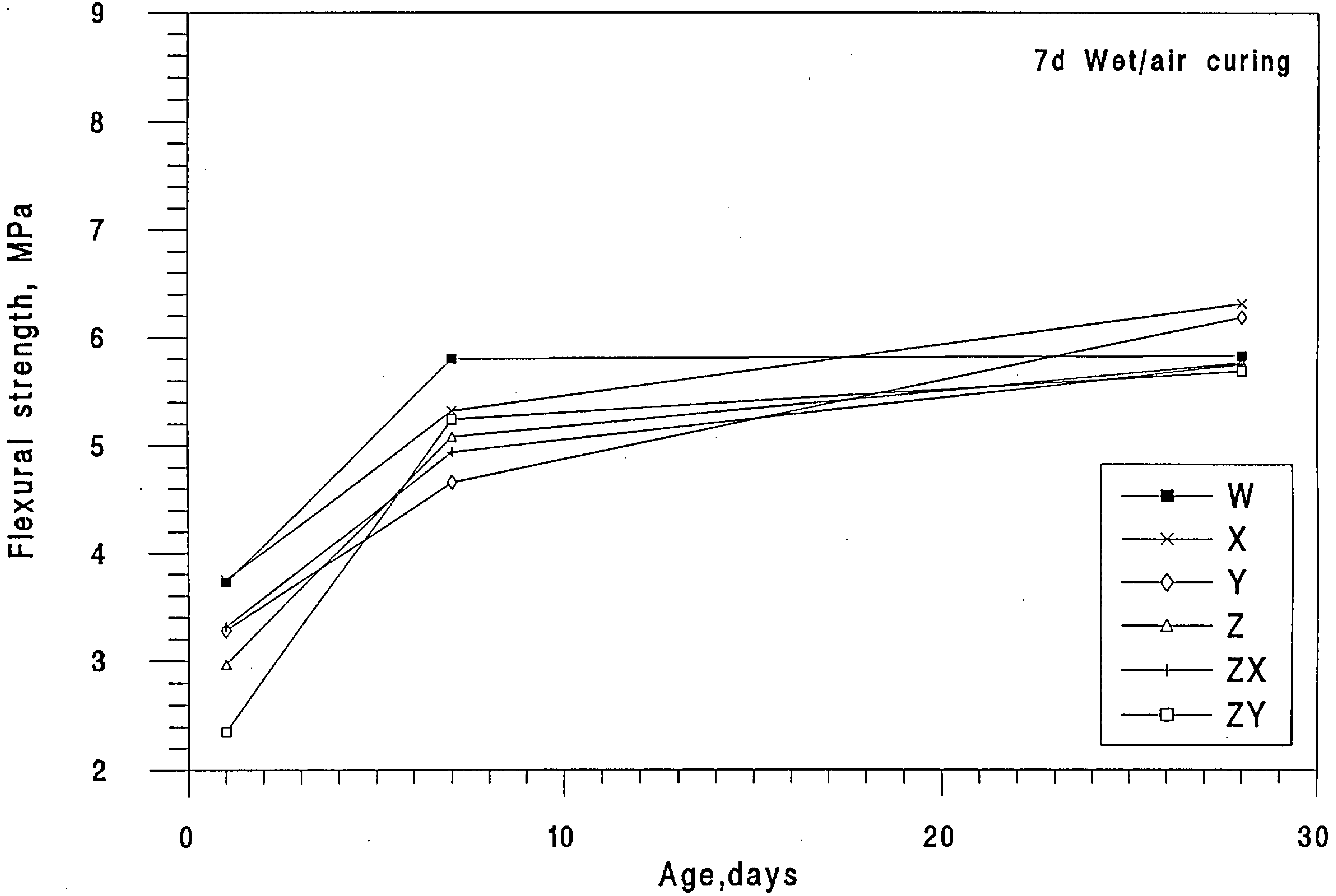


Figure 4.17 Effect of mineral admixures on 28 day flexural strength for mixes W,X,Y,Z,ZX and ZY

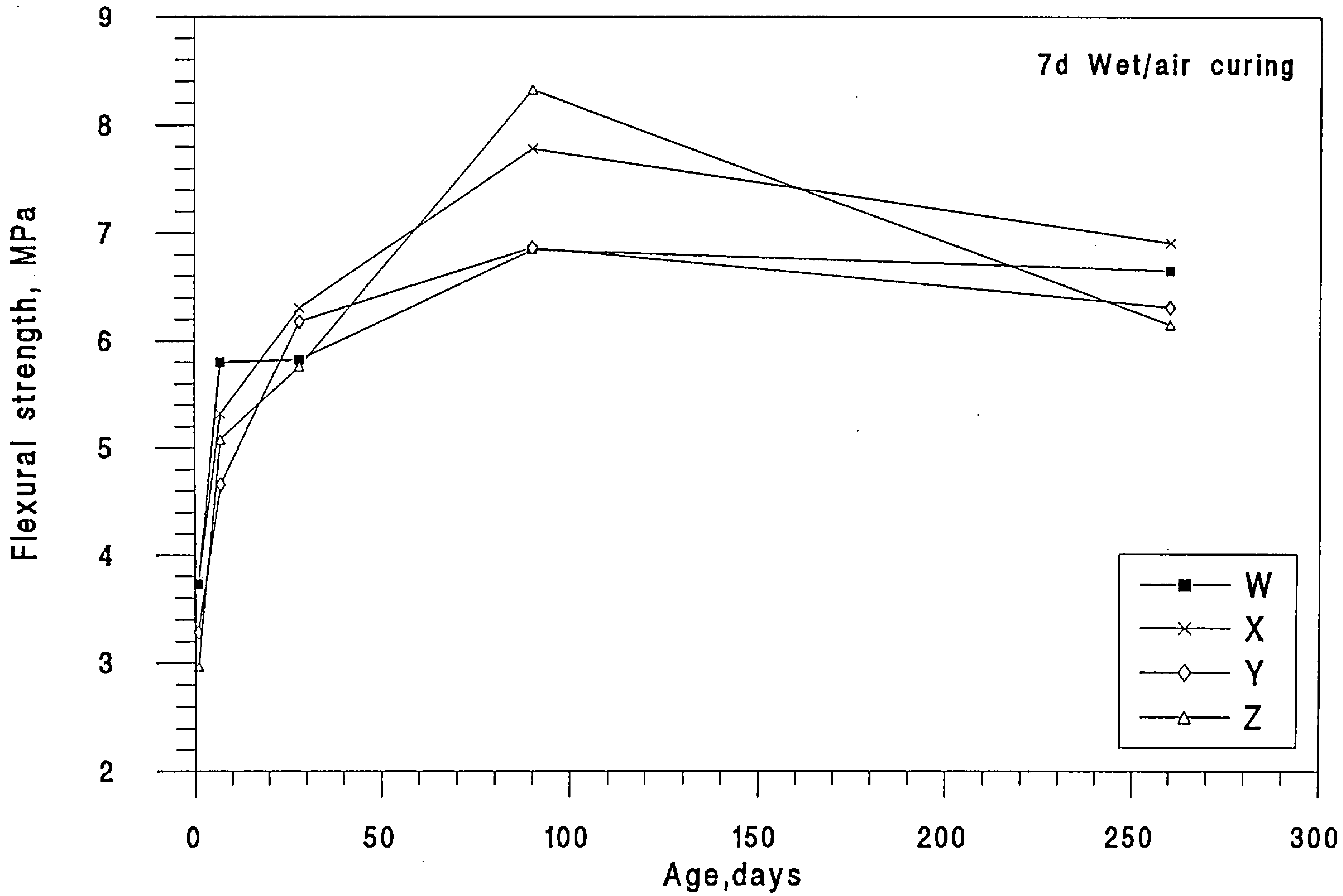


Figure 4.18 Effect of mineral admixures on flexural strength for mixes W,X,Y,and Z

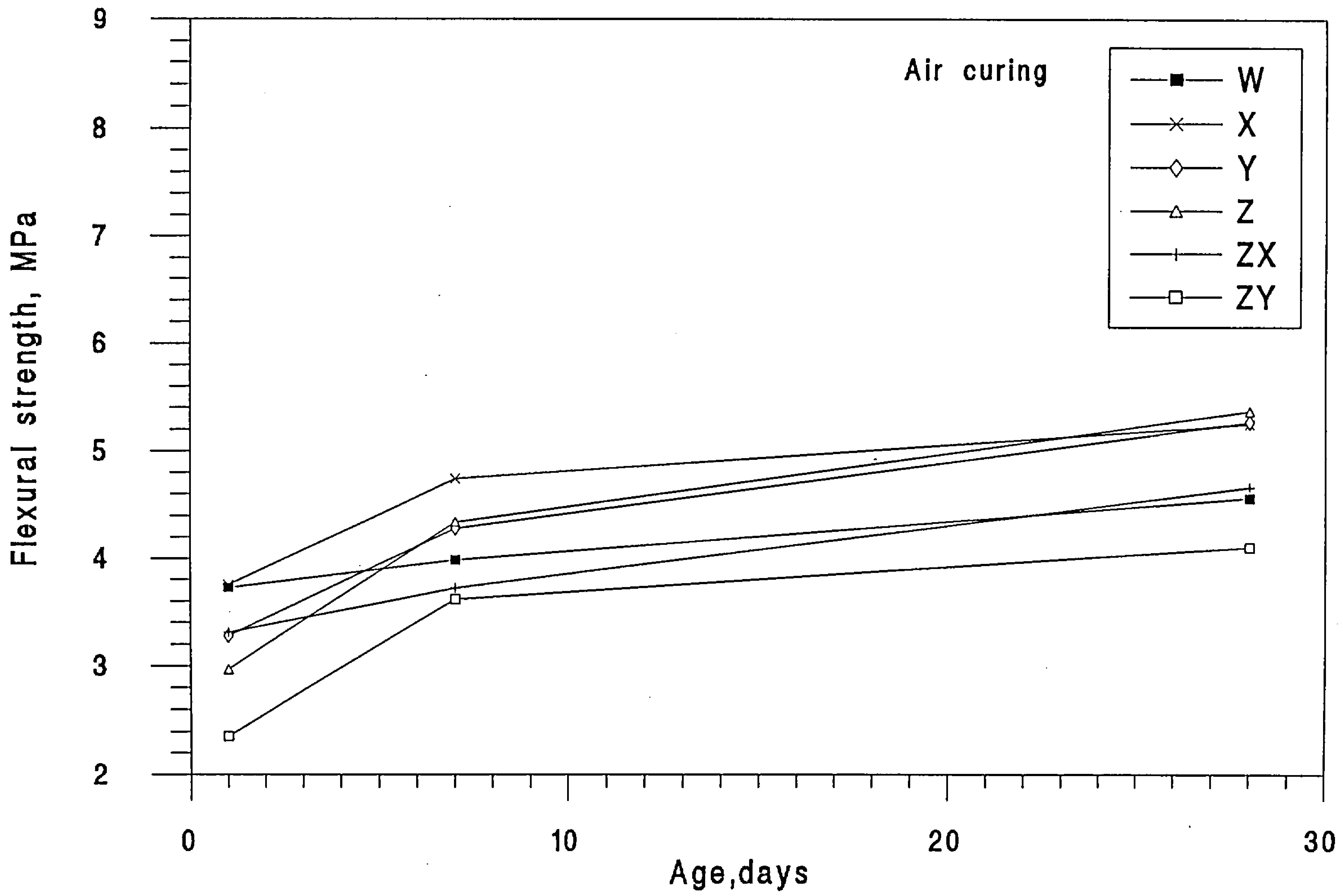


Figure 4.19 Effect of mineral admixutres on 28 day flexural strength for mixes W,X,Y,Z,ZX and ZY

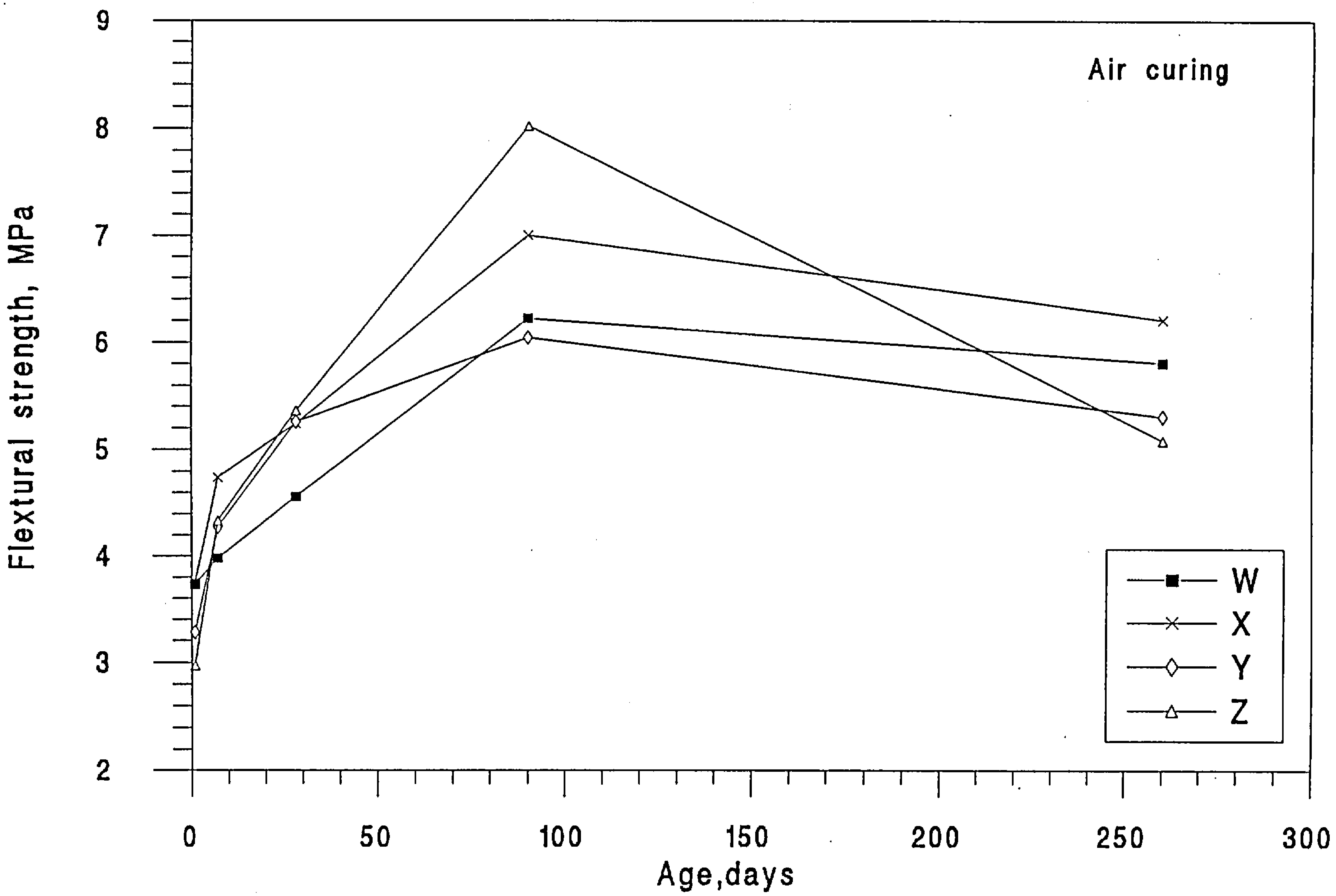


Figure 4.20 Effect of mineral admixures on flexural strength for mixes W,X,Y,and Z

days, both control and slag concretes exhibited similar strength values, 6.1 and 6.02 MPa whereas the 30 kg/m³ FA concrete exceeded these values by 23%, to give a strength of 7.42 MPa compared with considerably less strength for 80 kg/m³ FA concrete, 5.42 MPa. In another study Malhotra and Carette [55] reported a flexural strength of 5.8, 5.7 and 6.6 MPa for reference (330 OPC), control (50% OPC + 50% slag), and with 5% and 10% SF addition to the control concrete, respectively.

Swamy [48] also reported a strength of 6.84 and 7 MPa for 50 and 65% slag replacement concretes cured in fog room with total cementitious content at 400 and 420 kg/m^3 respectively. Hence it could be possible to produce higher flexural strength from slag mix adapted in this study with a higher amount of slag incorporation and by same silica fume content. At 90 days, the highest flexural strength of 8.5 MPa (141% of its 28 day strength) was obtained for concrete incorporating 80 kg/m³ slags followed by both 30 and 80 kg/m³ FA concretes, 7.3 and 6.74 MPa respectively (98 and 124% of their 28 day strength) whereas control concrete did not show strength development and gave a value of 6.16 MPa. Beyond 90 days, all concrete mixes showed strength loss, 6, 6.8, 6.56 and 6.88 MPa for W, X, Y and Z mixes respectively. The flexural strength values were rather similar for concretes Z and X compared with slightly less strength for Y mix while the control concrete has the lowest strength.

From the results, both 80 kg/m^3 slag and FA concretes have shown a considerable flexural strength development between 28 days and 90 days and even end up with higher strength values over their 28 day strength compared with control and 30 kg/m³ FA concretes. This could be due to relative high amounts of slag and FA, which is believed to be a result of the increased denseness of the paste [41], hence with relative large amount of slag and FA it could also be possible to extend the period of flexural strength retrogression.

The flexural strength development for concrete mixes W, X, Y, Z, ZX and ZY air cured following a 7 day water curing is shown in Figures 4.17 and 4.18. Mixes ZX and ZY have a total cementitious content of 450 kg/m³. All the concretes reached a maximum flexural strength at 90 days and indeed mixes W, X, Y and Z showed a considerable reduction in strength beyond this age as the continuously water cured concretes. Similar behaviour to that shown in Figure 4.16 was exhibited by these concretes at 1 and 7 day ages. The one day flexural strength of 165 kg/m³ slag concrete was surprisingly low, 2.37 MPa (63% of control concrete, which obtained 100% of its 28 day strength) whereas at 7 days it was almost the second highest in strength ranking, 5.24 MPa (90% of control). At the age of 28 days, both X and Y FA concretes showed slightly higher strength values, 6.3 and 6.18 MPa, compared with the control and the three slag concretes where there was no significant differences in their flexural strengths (Figure 4.17). The relative low values for slag concretes observed might be due to insufficient water for hydration process because of 7 day curing. However the results of ZY mix indicates the pozzolanic activity of slag at this stage and confirms the previous discussion, that with relative high slag content similar flexural strengths to that of control and other mixes could be obtained besides the possibility of continuing the strength development in later ages provided there is enough curing period. At 90 days, the control and 80 kg/m^3 FA exhibited similar strength values 6.84 and 6.86 respectively, whilst the 80kg/m^3 slag concrete registered the highest strength value, 8.32 MPa (144 of it 28 strength) (122% of control) compared with 7.3 MPa (114 of control) for 30kg/m^3 FA concrete. The order of these strength values was much the same as those observed at 90 days for compressive strength. At 260 days surprisingly mix Z exhibited the lowest flexural strength 6.14 MPa (107% of its 28 day strength) compared with 6.64, 6.9 and 6.3 Mpa for W, X, and Y mixes respectively. In fact both control and 30 kg/m^3 FA concrete showed better strength values corresponding to their strengths at continuous water curing, and still they showed higher strengths over their 28 day strength.

A similar comparison for flexural strength development is presented in Figures 4.19 and 4.20 for the same concretes air cured immediately after demolding at 24 hours. The development of flexural strength is similar to that of 7d wet/air cured concretes but with lower strength values due to the influence of the bad curing. It reflects somewhat the trend of compressive strength development under the same curing regime. The one day flexural strengths were the same as that shown in Figure 4.17, some differences were observed at the age of 7 days where mix X exhibited the highest strength value 4.74 MPa compared with the other mixes. Control concrete strength were higher than both 125 and 165 kg/m^3 slag concretes, 3.72 and 3.62 MPa, but was lower than the strength of 80 kg/m^3 FA and slag concretes, 4.28 and 4.34 MPa respectively. The increase of all concrete mixes at 7 day age was in the order of 80-90% of their 28 day strengths. At 28 days, the X, Y, and Z mixtures were close to each other, showed almost equal strength values and had higher strength than both the control and ZY mixes (Table 4.8) while the ZX mix appears to be the weaker concrete (Fig 4.19) indicating more than the other concretes the adverse effect of no curing on strength development for a relative high slag content. This is confirmed by the compressive strength results up to 28 days for ZY mix (Table 4.2) which show a pattern similar to that observed now. At 90 days, however, mix Z obtained the largest strength 8.02 MPa (130% of control) (150% of its 28 day strength) compared with mixture Z, 7 MPa (115% of control) whereas mix Y about approached the value of control mix. Again beyond 90 days all concretes began to show a loss in flexural strength, surprisingly the 80 kg/m^3 slag was the lowest (95% of its 28 day strength) clearly showing the adverse effect of drying environment on slag concrete strength. As for control concrete slight loss was observed (127% of its 28 day strength) compared with 118 and 100% of their 28 day strength for mixes X and Y, respectively. In other words it can be said that the adverse effect of no curing is proportional to the amount of mineral admixtures added and the effect can be more pronounced with slag.

4.4.3 Relationship of Flexural Strength to Compressive Strength

Fig 4.21 shows the variation of flexural strength with compressive strength for concrete mixes cured in wet, 7d wet/air and air curing regimes respectively. Linear regression analysis was carried out between the compressive and flexural strengths of each cured condition mixes. A number of empirical formula have been suggested to relate the flexural strength (f_f) and compressive strength (f_c) strengths. Most are of the type

$$f_f = kf_c^n$$

where k and n are coefficients which depend on the method of testing, size of specimen, the shape and surface texture of aggregate, and the moisture condition of the concrete [3]. The regression analysis gave the following equations and correlation coefficients

$f_f = 0.71fc^{0.527}$ (wet) (r=.969)
$f_f = 0.76fc^{.505}$ (7d wet/air) (r=.966)
$f_f = 0.80fc^{.816}$ (air) (r=.903)

From the figure and data, it can be seen that for all mixes and curing conditions the flexural strength is reasonably well correlated with compressive strength. However, due to the adverse effect of air curing on strength development, better correlation was found for concretes continuously cured in water and for those that were 7d wet-cured. The ratio of the two strengths depends on the general level of strength of the concrete; the higher the compressive strength, the lower the ratio of flexural to compressive strength (Table 4.8). Generally the ratio decreases as the age of curing increases; at one day age the ratio was found to be the highest for all mixes; mix ZY had a ratio of 25%, compared with 20, 19, 18, 16 and 14% for mixes ZX, Z, Y, and W respectively, whereas at 7 days age the ratio of mix ZY was of the same order as the control mix. This shows that at an early age the flexural/compressive strength ratio for the control mix was lower when no mineral admixtures were present in the concrete mixtures particularly at high replacement

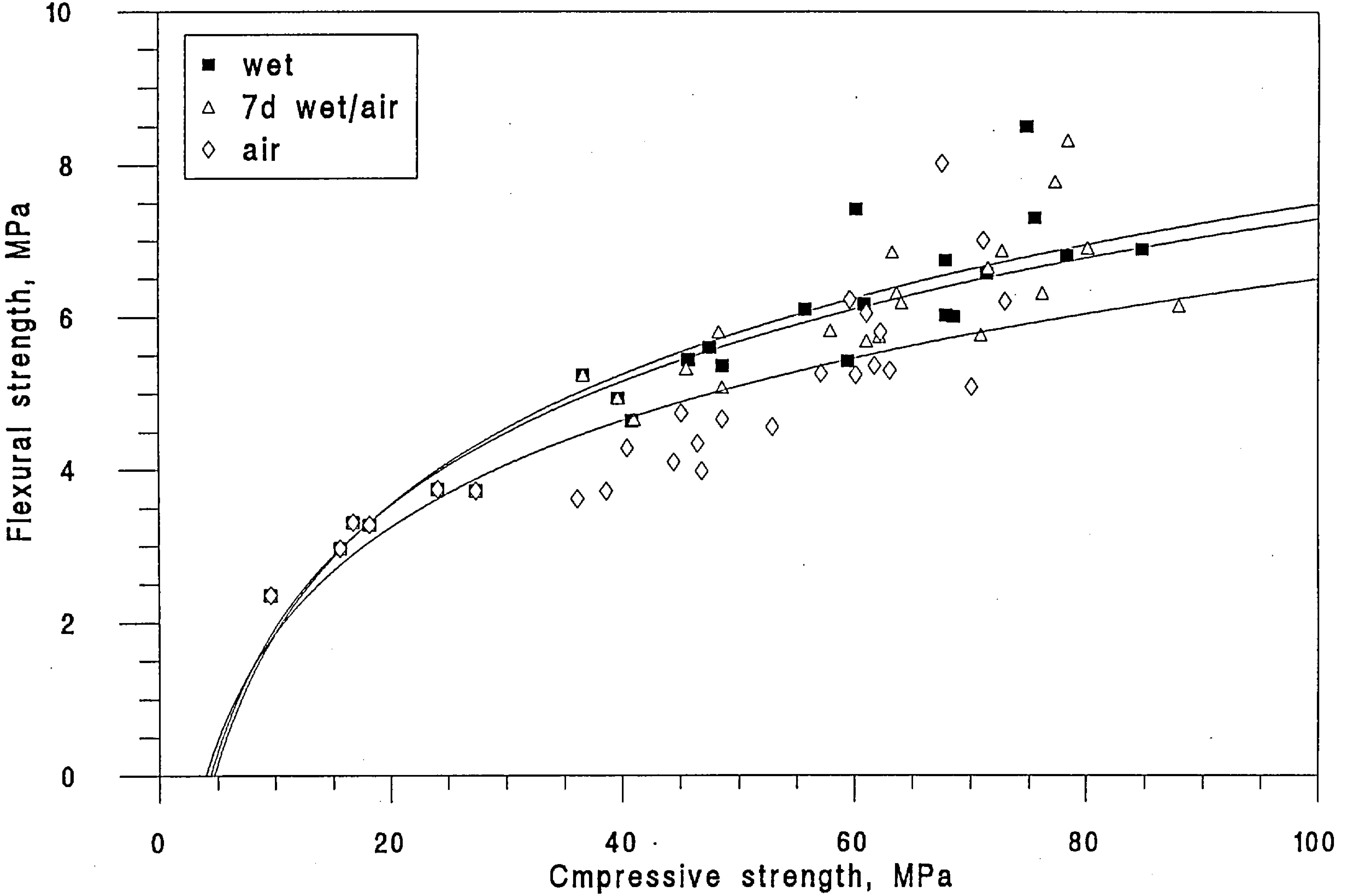


Figure 4.21 Relationship between flexural strength and compressive strength

level such as in mix ZY. At 28 days compressive strength level of about 55 MPsa to 68 MPa the ratio for all mixes varied from 9 to 12%. At 90 to 260 days about 10% ratio was obtained for all mixes under different curing conditions, mix Z at 260 days showed a slightly lower ratio because of its very high compressive strength. However looking to each age beyond 7 days no significant difference in ratio was observed between wet, 7d wet/air- and air- cured mixes. The flexural to compressive strength ratio of 7d wet/air- and air-cured mixes follow the same patterns as for wet cured ratio (Figure 4.21).

Malhotra and Carette [55] reported data on various SF/slag concretes; it was found that flexural/compressive strength ratio at 28 days varied from 13 to 17. The compressive strength values of all three mixes were lower than that obtained in this study. Khayat and Aitcin [83] reported data analysed by Loland and Gjorv on the ratios of tensile-to-compressive strengths of concretes tested after 3 months of moist curing and other air-cured concretes which received 7d of initial wet curing and then were tested at approximately 1 year of age. The findings suggested that the ratios of either direct tensile or flexural strengths to compressive strengths of dry-cured concretes containing SF were comparable to those of wet-cured concretes also made with SF.

Khayat and Aitcin [83] as quoted by Johansen, also reported that concrete containing 5% SF and cured in air for 3 years can have a flexural-to-compressive strength ratio comparable to that of a similar concrete without SF. Similar results were observed with concrete containing 11% SF replacement and water reducer. On the other hand, similar concrete containing 11% SF and no water reducer and other concretes containing 25% SF replacements and made with or without water reducers were found to have lower flexural-to-compressive strength ratios than those of non SF concretes.

Similar findings to the results of this study were observed by Neville and Brooks [3]. They compared continuously wet-stored concrete with concrete cured and then stored in a dry environment. Under these circumstances, the compressive strength of drying concrete was greater than when continuously wet-stored; the splitting and direct tensile strengths were not affected in a similar manner. However, the flexural strength of drying concrete was lower than that of wet concrete, they attributed this probably because of the sensitivity of this test to the presence of moisture gradients and the resulting shrinkage cracks.

In general there are several factors which affect the relationship between compressive strength and tensile strength. Not only the curing condition and age but also the characteristics of the concrete mixture, such as water/cementitious ratio, type of aggregate, and the admixtures affect of this ratio to varying degrees.

4.5 Dynamic Modulus of Elasticity

The dynamic modulus of elasticity was determined non-destructively according to BS 1881: Part 109: 1990 on a daily basis for the first 28 days and twice a week afterwards. The average 1, 7, 28, 90 and 260 day dynamic modulus results for the six mixes are presented in Table 4.9. The effect of wet, 7d wet/air and air curing conditions (as before) were investigated and are illustrated in graphical form in Figures 4.22 to 4.26.

The figures show that the highest values of dynamic modulus for all mixes were obtained under continued wet conditions of curing followed by specimens cured under 7d wet/air and air curing conditions, respectively. This increase in modulus with increase in age is expected because the hydration process is enhanced for mixes continuously kept underwater. Similar results were observed by others [48,88].

The modulus values of FA/SF and slag/SF wet-cured specimens were higher by about 15 and 20% than 7d wet/air- and air-cured specimens, respectively, at the age of 260 days. Davis and Troxell observed that the modulus of elasticity of concrete was 12 to 30% higher for wet concrete than dry [89].

Between 1 and 3 day age rapid increase in dynamic modulus was observed under the three curing conditions, the differences were slightly less in air cured specimens.

The greatest increase in modulus occurred between 1 and 7 days; all wet-cured specimens registered 87% of their 28 day modulus whereas all 7 day wet/air and air-cured specimens registered 96% of their 28 day modulus. The increase beyond 7 days was more gradual and much less, and the general shape of modulus development under different curing conditions was the same for all mixes. These trends could be explained by the different rates of hydration, the availability of water for hydration and the presence of waterfilled pores in the different mixes [48]. At the age of 28 days, the 7d wet/air- and air-cured specimens exhibited their largest modulus values and did not show any further improvement in modulus development beyond this age whilst the wet-cured ones continued showing increases in the dynamic modules.

The adverse effect of air curing, continued drying, on dynamic modulus was pronounced at 7 days and beyond, when compared with wet modulus a significant drop in modulus of

Table 4.9 Development of dynamic modulus of elasticity with age under various curing conditions

Mix type	curing condition	Compressive strength MPa (28-day)	Dynamic modulus GPa (28-day)	Compressive strength MPa (90-day)	Dynamic modulus GPa (90-day)	Compressive strength MPa (260-day)	Dynamic modulus GPa (260-day)
W	Wet curing	55.7	42.8	60.8	44.6	68.5	46.0
X		60.1	42.1	75.5	44.0	78.3	45.3
Y		59.4	41.0	67.8	43.0	71.4	44.4
Z		67.9	42.7	74.8	44.6	84.8	45.7
ZY		61.6	44.0	69.7	47.2	-	-
W	7d wet/air curing	57.9	42.8	63.2	43.3	71.5	43.6
X		63.6	39.7	77.3	39.8	80.1	39.3
Y		64	38.6	72.7	38.7	76.2	38.3
Z		70.9	40.4	78.4	40.8	88.0	40.0
ZX		62.1	41.1	-	-	-	-
ZY		61.0	40.1	72.1	-	-	-
W	air curing	52.9	40.1	59.6	40.4	62.2	40.8
X		60.1	38.1	71.1	38.2	73.0	38.1
Y		57.1	36.3	61.0	36.5	63.0	36.6
Z		61.7	37.9	67.5	38.6	70.1	38.1
ZX		48.6	37.7	-	-	-	-
ZY		44.4	36.2	52.0	38.2	-	-

Table 4.10 Dynamic modulus difference between one and seven days of wet and air cured concrete

Mix	Compressive strength, MPa			Dynamic modulus, GPa			Difference in modulus of 1 and 7 days	
Curing	Wet		Air	Wet		Air	Wet	Air
Age	1 day	7 days	7 days	1 day	7 days	7 days	1d-7d	1d-7d
W	27.3	47.5	46.8	35.4	40.4	39.2	5.1	3.9
X	24.0	45.7	45.1	31.1	38.8	37.1	7.1	5.2
Y	18.1	40.8	40.4	29.0	37.0	34.8	8.0	5.5
Z	15.6	48.6	46.5	28.5	38.3	36.4	9.8	8.1
ZX	16.7	39.6	38.6	28.0	38.7	36.0	10.7	8.4
ZY	9.6	36.6	36.1	25.0	37.6	34.9	12.6	10

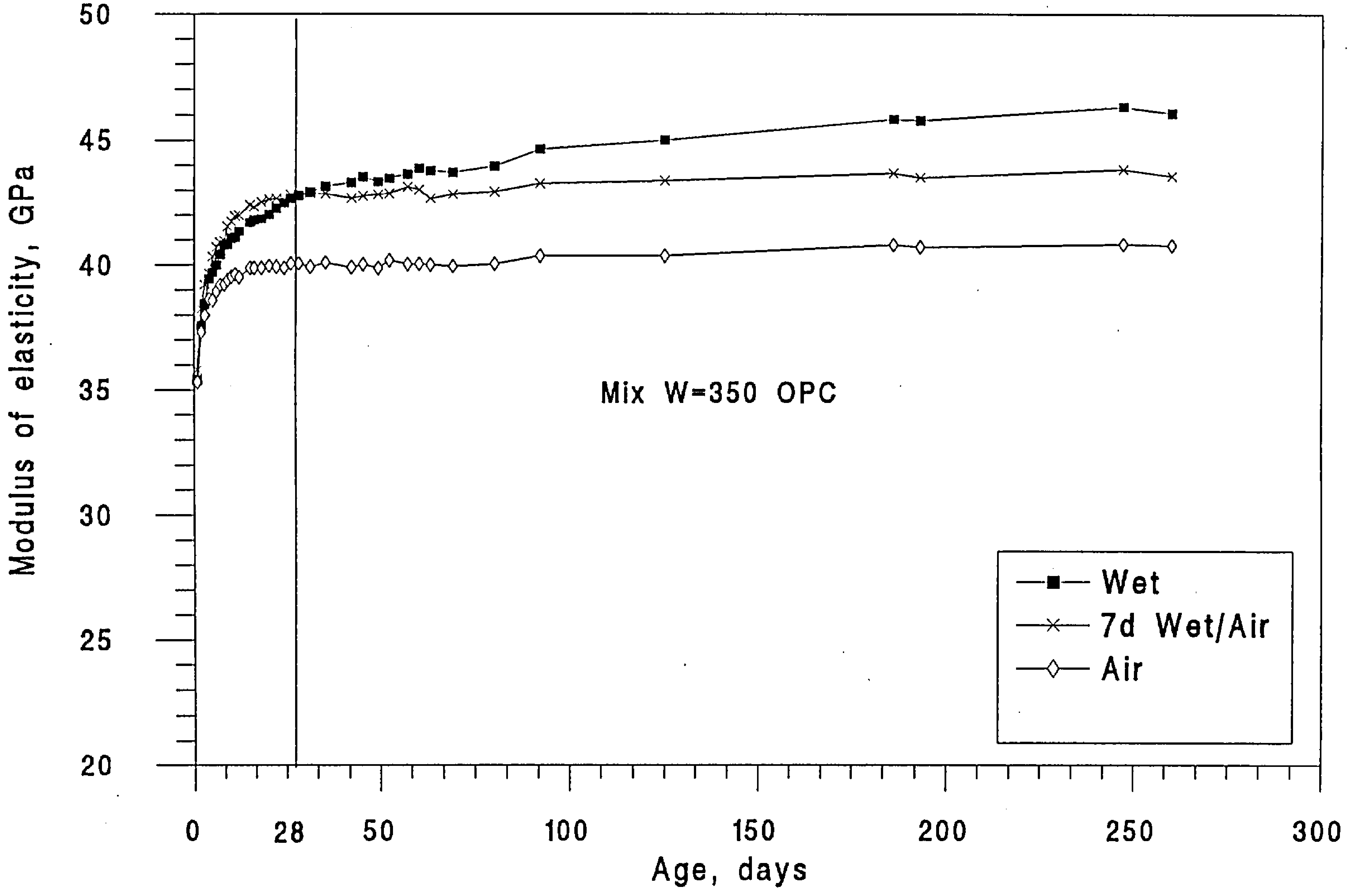


Figure 4.22 Effect of curing on dynamic modulus of elasticity for control mix W

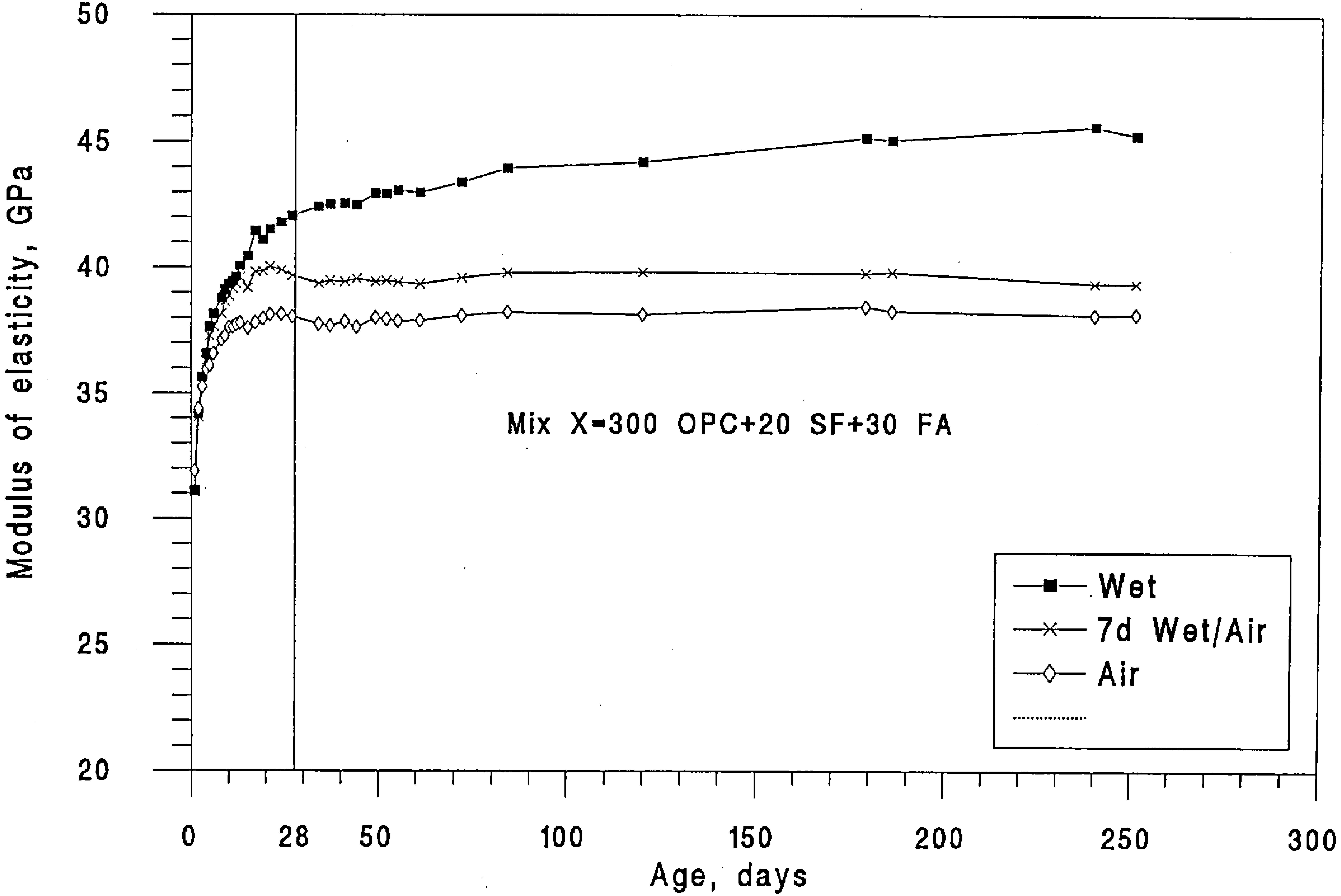


Figure 4.23 Effect of curing on dynamic modulus of elasticity for mix X

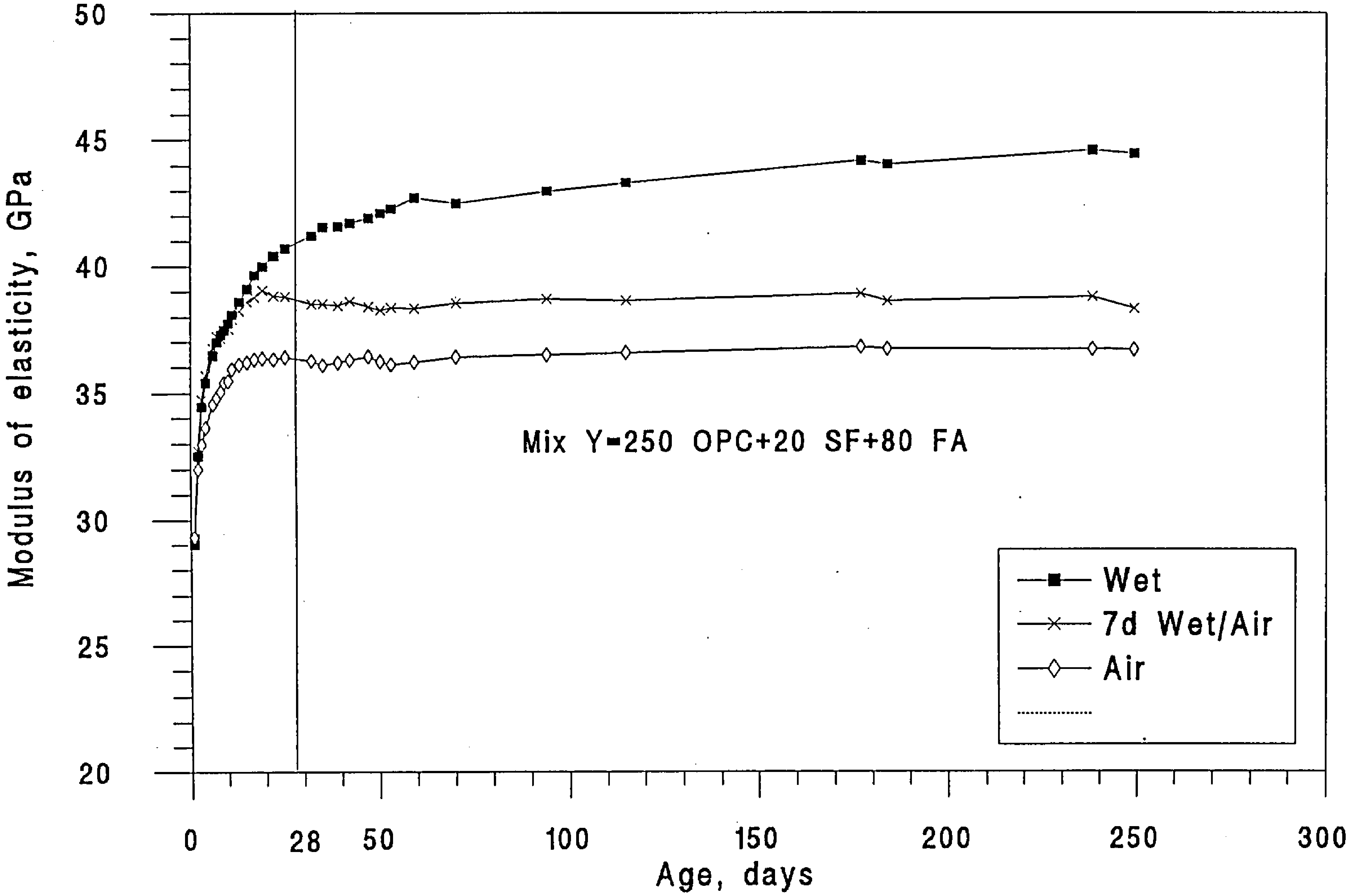


Figure 4.24 Effect of curing on dynamic modulus of elasticity for mix Y

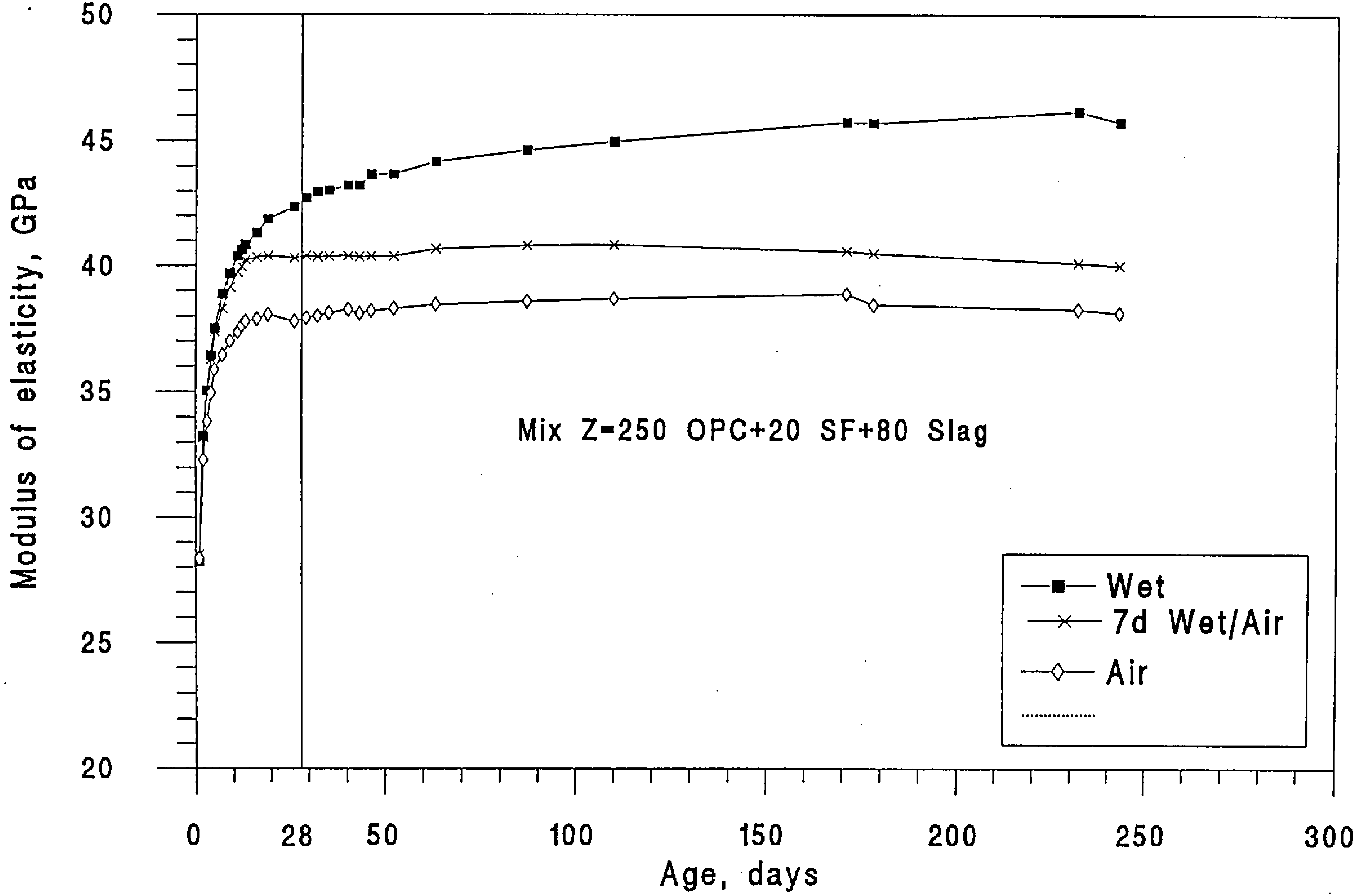


Figure 4.25 Effect of curing on dynamic modulus of elasticity for mix Z

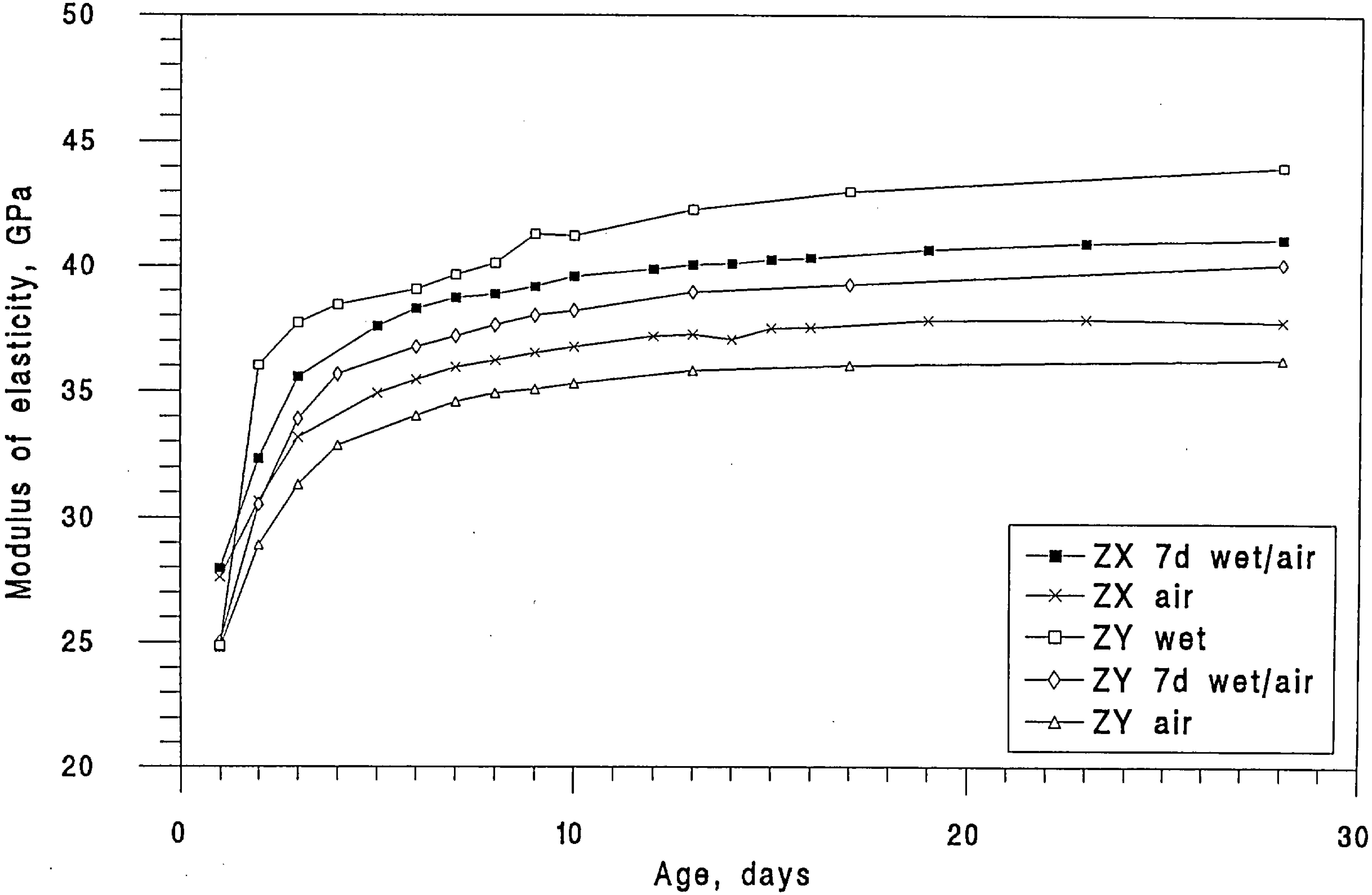


Figure 4.26 Dynamic modulus for mixes ZX and ZY

air- cured specimens was found. At end of testing the loss between wet- and air-cured specimens of FA/SF and slag/SF mixes varied between 15 and 20%, for the control mix, it was 10%. The results also show that with 7d wet/air and air curing the modulus tend to decrease at later ages. It is suggested that shrinkage induced microcracking is possibly the mechanism responsible for the reduction of the modulus on drying [48]. Also this drop in the dynamic modulus is also probably due to moisture/stress gradients and removal of interlayer water [50].

Haque however, as cited by Al-Mudaiheem [47], attributed the reduction of dynamic modulus to microcracking and irreversible changes in the structure of the hardened cement paste on first drying. On the other hand, Swamy [48] stated, that during the rapid drying stage which corresponds to the removal of moisture from capillary channels - there is a rapid decrease in the dynamic modulus, which slows down as the rate of differential shrinkage cracking stabilises. However,the reduction in dynamic modulus on drying observed in this study could be due to microcracking and removal of interlayer water . On the other hand whether the reduction of the dynamic modulus caused by drying is reversible or not, is another issue that could be discussed.

4.5.1 Effect of Curing

Figure 4.22 shows the development of dynamic modulus of elasticity with age for control mix under three curing conditions. The figure shows that at the age of one day the modulus value was about the same, 35.5 GPa (85% of the 28 day modulus) whereas at the second day of curing the values jumped to 37.6, 38.2 and 37.3 GPa for wet, 7d wet/air- and air-cured specimens, respectively showing an increase of 5% over their 28 day modulus and thereafter a steady low degree of gain in modulus was observed and the corresponding modulus values were 40.4, 40.9 and 39.2 GPa at 7 days of age. In fact at this age 90% of the value in 9 months was registered for wet-cured specimens and a value of 95% for both 7d wet/air- and air-cured specimens. In other words most of the modulus development took place at very early ages of curing (1 to 3 days) with very small differences between dynamic moduli of different cured specimens. However, the effect of curing was pronounced after 7 days on air- cured specimens compared with both wet and 7d wet/air cured specimens while after 14 days this effect was observed between the wet and 7d wet/air- curing conditions (Figure 4.22).

At the age of 28 days, wet- and 7d wet/air- cured specimens exhibited similar modulus values 42.8 GPa compared with 40 GPa for air-cured ones. On the other hand at this age both 7d wet- and air-cured specimens obtained about 100% of their 9 month modulus compared with 93% for wet-cured specimens. Further, the increase of modulus for 7d wet/air- and air-cured specimens with age and curing exhibited a plateau at later ages whereas the wet-cured specimen still showed modulus development. At the age of 260 days the effect of different curing regimes on dynamic modulus could be readily seen, the wet cured specimens showed better performance than the other cured specimens as well the 7d wet/air compared with air-cured ones. The modulus of wet-cured specimens was higher by 2.5 and 5.3 GPa than 7d wet/air- and air-cured specimens respectively, and this shows the adverse effects of no curing, which is more pronounced at later ages rather than early ages.

A similar comparison for development of dynamic modulus is presented in Figures 4.23 and 4.24 for the 30 and 80 kg/m^3 FA/SF mixes cured in wet, 7d wet/air and air curing conditions. Comparing both figures, the modulus development behaviour of 30 kg/m^3 FA mix under the three curing conditions followed the pattern of 80 kg/m^3 FA mix with small differences between their modulus values. In general, regardless of curing, sudden rise in dynamic modulus at very early ages was observed. At 7 days, both wet- and 7 day wet/air-cured specimens obtained similar modulus values 38.8 and 38.2 GPa compared with 37.1 GPa for air-cured ones. The same was said for 80 kg/m^3 mix where the modulus value was 37 GPa for wet- and 7d wet/air-cured specimens compared with 34.8 GPa for air-cured ones. For both mixes, at this age the wet-cured specimens obtained about 85% of the 9 month modulus whereas the 7d wet/air- and air-cured specimens showed modulus development of 96% of their 9 month modulus. In both mixes the 7d wet/air-cured specimens exhibited their highest modulus values at 21 days, 40 and 39 GPa for mixes X and Y respectively. At 28 day age of the modulus of the 7d wet/air- and air-cured specimens of both mixes were found to equal or very slightly exceed the 9 month values compared with a corresponding value of 90% for wet-cured specimens. As a consequence it can be said that drying caused by air curing or after 7 day wet curing might lead to a restricted hydration in concrete and thus stopped the modulus development. Therefore keeping concrete wet during most of its hydration period has a far reaching effect on producing a good quality concrete which has high dynamic modulus due to the development of a dense internal structure.

Beyond 28 days the wet-cured specimens continued to obtain higher modulus values whereas no further development in modulus of 7dwet/air- and air-cured specimens was observed. The modulus of wet-cured specimens was higher by 6 GPa and about 7.5GPa than 7d wet/air- and air-cured specimens respectively.

The effect of the three curing conditions on development of dynamic modulus ofslag/SF concretes (Z, ZX and ZY) is shown in Figures 4.25 and 4.26. Similar trends were observed for 1, 3, 7 and 28 days with wet-cured specimens having the highest modulus, and the air- cured one having the smallest values. This might probably reflect a trend of slowing down the hydration reactions, after a few days of curing. At 7 days, the 7d wet/air- and air-cured specimens of the three mixes obtain a similar modulus development, 96% at their 28 day modulus, but the absolute dynamic modulus values of the former specimens were higher by 5 to 10% than the later ones. 38.3, 38.7 and 37.6 GPa for mixes Z,ZX and ZY respectively compared with corresponding air cured values of 36.4, 35.9 and 34.9 GPa. This difference between 7d wet/air- and air-cured modulus values remains about the same as modulus increases with age, up to 28 days. Thus it can be said that there is an adverse effect because of no curing but this effect seems to be the same on each of the slag mixes, and the marked improvement in wet-cured specimen modulus is due to a direct consequence to continued hydration process which produced intergrown micro structure in concrete. At 28 days, the wet-cured specimens of mix Z obtained modulus value of 42.74 (93% of its 9 month modulus) compared with 40.4 and 37.9 GPa for 7d wet/air- and air-cured specimens respectively (100% of their 9 month modulus). Beyond this age as usual no increase in dynamic modulus was observed for the 7d wet/air- and air-cured specimens compared with a relative higher modulus values of 45.7 GPa for wet cured specimens at the age of 260 days.

On the other hand, the 7 day wet/air-cured specimens of ZX and ZY were still showing better performances than air-cured ones, an increase of 10% was obtained.

4.5.2 Effect of Cement Replacement Materials

Dynamic Modulus at 1 to 7 days

In general, regardless of curing condition, a rapid increase in dynamic modulus of elasticity was observed in all mixes. The gain of modulus of slag/SF mixes was substantially higher for the period (0-7 days) followed by that of FA/SF mixes and then by that of the control mix, but the absolute modulus values were less than the control mix (Table 4.10 and Figure 4.27-a). The same mixes, wet and dry cured, show a pattern of behaviour similar to compressive strength development up to this age. In fact the very low modulus values at the age of one day of slag and FA concretes, varying between 15 to 30%, compared with modulus of control mix could be attributed to: (1) SF which makes some contribution to the strength (hence to the modulus) of a given concrete mixture at very early ages of hydration (viz, 1 to 3 days), significant contribution during the first 2-4

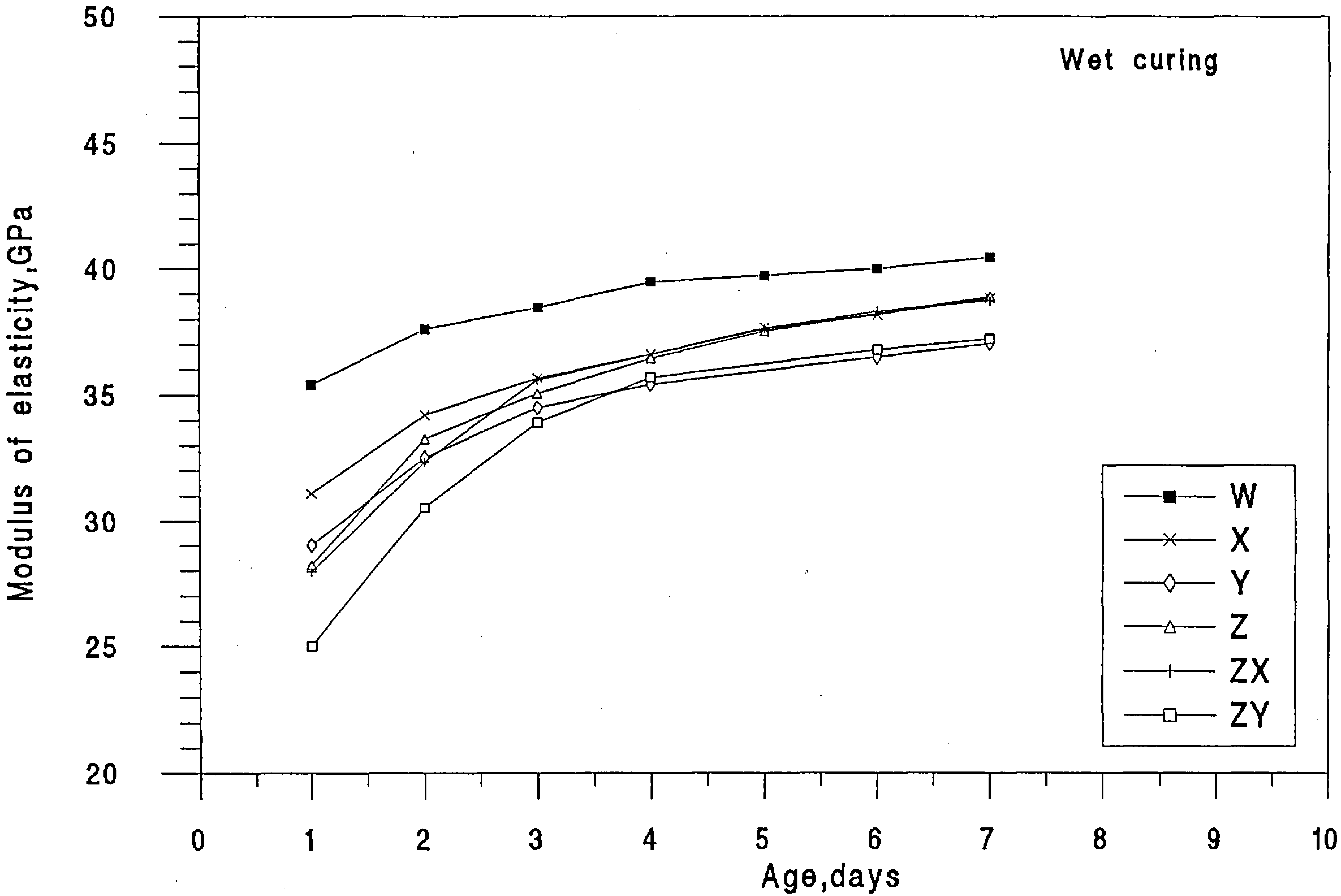


Figure 4.27-a Dynamic modulus differences between W,X,Y,Z,ZX,and ZY mixes for period,1 to 7d

weeks, and relatively little contribution thereafter [34], and (2) FA and slag with their coarser particles and low specific surface retards the development of engineering properties of concrete at very early ages and make little strength and modulus contribution at this age (viz, 1 to 3), their considerate contribution comes at later ages (after 2 to 3 weeks).

At 7 days, the modulus values were 40.4, 38.8, 37, 38.9, 38.7 and 37.6 Gpa for mixes W, X, Y, Z, ZX and ZY respectively, where the difference between control and these mixes varied between 4 to 8% only. The 7 day values of moduli were very similar for X, Z and ZX mixes and were comparable to Y and ZY. As a result it can be said that the rate of gain of modulus at early ages for FA and slag concretes increases far more with the addition of SF than an equivalent portland concrete. The substantial gain in modulus at early ages of these concretes incorporating FA or slag and SF may suggest an early start of the pozzolanic reaction due to the use of SF and may also be partially due to its role as an effective filler at an early age resulting in a denser matrix structure. Djellouli et al [90] explained this higher gain in modulus of elasticity for slag/SF concrete by the early role played by SF as an activator, on the one hand, and as a non contributor due to its complete transformation in to dense C-S-H gel at 28 days, on the other. Similar to the results reported here, he obtained modulus values of 39.1 and 41.5 GPa at 7 and 28 days respectively for a high strength concrete mix of 300 OPC + 150 slag + 50 kg/m^3 SF with water/binder ratio of 0.27.

In fact elastic modulus of concrete is not directly influenced by the incorporation of a mineral admixture into a concrete mixture. Instead, this property of concrete is largely influenced by the aggregate (both content and stiffness) and by the concrete strength (w/b and curing). Therefore, to the extent the strength development in a concrete is affected by the incorporation of mineral admixture, its elastic modulus will also be affected, and in general when the strength is reduced, the elastic modulus is also reduced [81].

On the other hand, the gain in modulus of air-cured specimens was approximately the same to that of wet-cured ones for the period (1 to 7 days) for the control and the other mixes. At 7 days, control mix exhibited the highest modulus value 39.2 GPa compared with 37.1, 34.8 36.4, 35.6 and 34.9 GPa for X, Y, Z, ZX and ZY mixes respectively. X and Z mixes of the same cement and FA or slag content have about similar values of modulus for similar compressive strengths. Mixes Y, ZX and ZY were much affected by air curing compared to the control and other mixes, this might be due to a relative high slag and FA incorporation. However, the most important influence on changes of elastic modulus is water curing. Prolonged air drying, particularly at early ages, can substantially reduce the stiffness values at later ages, but these adverse effects can be reduced by appropriate mix proportioning [91].

Dynamic modulus at 28 days beyond

Table 4.10 and Figures 4.27 to 4.29 present relevant data: each figure represents dynamic modulus of elasticity for the various mixes considered in this study under one of the curing conditions.

Variations of dynamic modulus with age of mixes W, X, Y, Z and ZY were shown in Figure 4.27, under wet curing condition at 20°C. The figure shows that all mixes continue to show development in dynamic modulus with increase in age, and that mixes W and Z exhibited almost similar modulus values at all ages which were higher compared with mixes X and Y, however mix ZY registered the highest modulus value. Mix Y exhibited the lowest modulus values, for example at 28 days, the modulus values were 44.0, 42.8, 42.7, 42.2 and 41 GPa for mixes ZY, W, Z, X and Y, respectively, and at the age of 260 days the corresponding values were 46.0, 45.7, 45.3 and 44.4 GPa. It appears also from the Figure 4.27 that the rate of modulus increase was low after the age of 28 days, an increase of about 8% over their 28 day modulus was achieved by all mixes for a compressive strength increase of 20 to 30%. In fact even the 28 day as well as 90 and 260 days strength of X and Y FA mixes were higher than the control, they exhibited slightly lower modulus values. This means that the effects of FA on modulus of elasticity were not as significant as the effects of FA on strength, similar effects were reported by Jain in ACI committee 226[40] where he concluded that cement and aggregate characteristics will have greater effect on modulus of elasticity than the use of FA. Ghosh and Timusk [52] studied FA concretes, proportioned for equivalent 28 days strength, over a range of nominal strength values and he concluded that for all strength levels the modulus of elasticity of FA concrete was generally similar to reference concrete. In regard to slag, others [19,52] found that modulus of elasticity of slag concretes would be similar to that of non slag concrete. Similarly, no significant differences between modulus of elasticity of concrete with and without SF were observed [56]. However it is noteworthy to know that with same cement content modulus of ZY mix with 165kg/m^3 slag was higher than modulus of mix Z with 80kg/m^3 slag.

The data reported by Malhotra et al [56] show a similar trend to the data shown here: with 47GPa (28d compressive strength) concrete mixtures, both with and without 50%

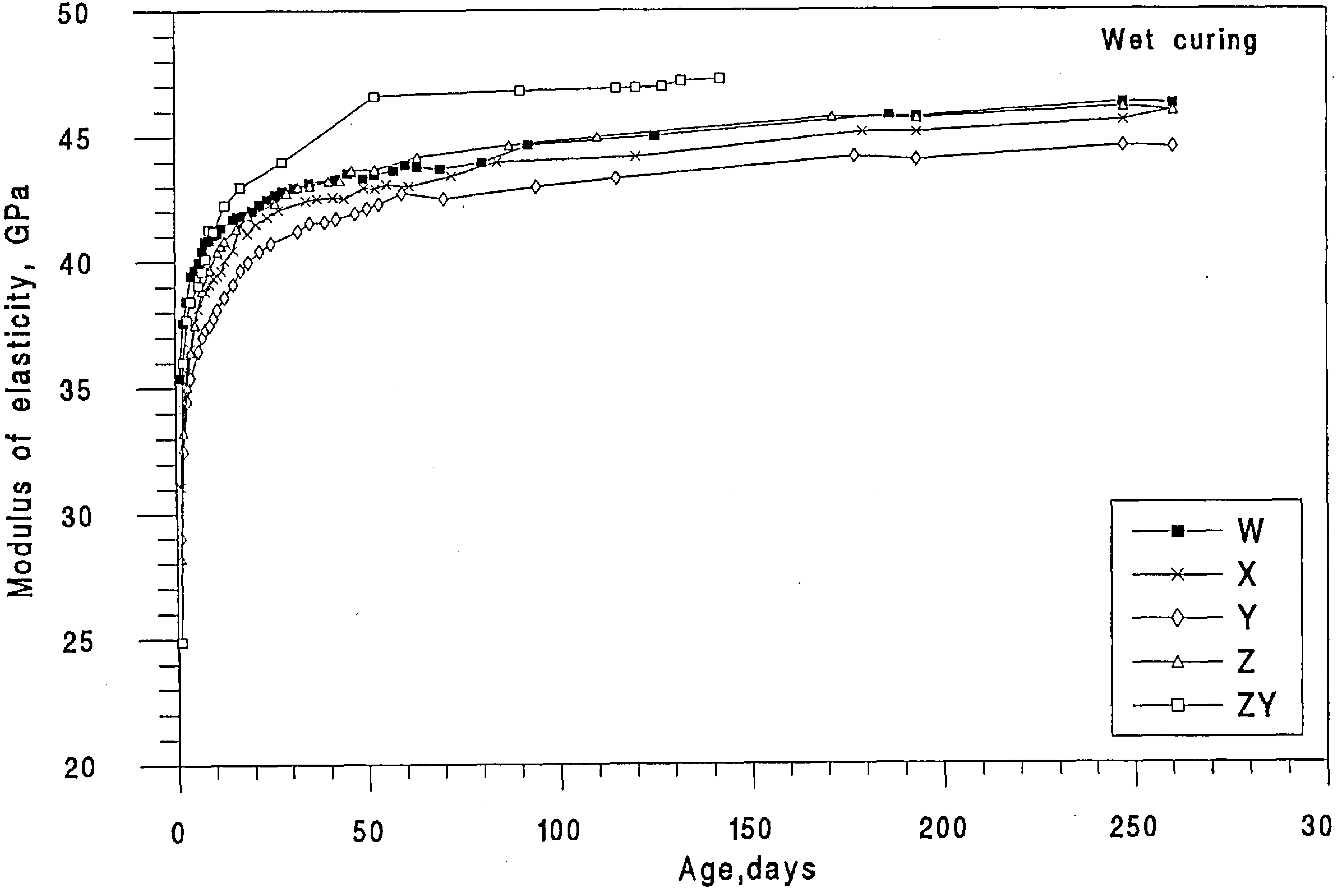


Figure 4.27 Effect of mineral admixtures on dynamic modulus for mixes W,X,Y,Z and ZY

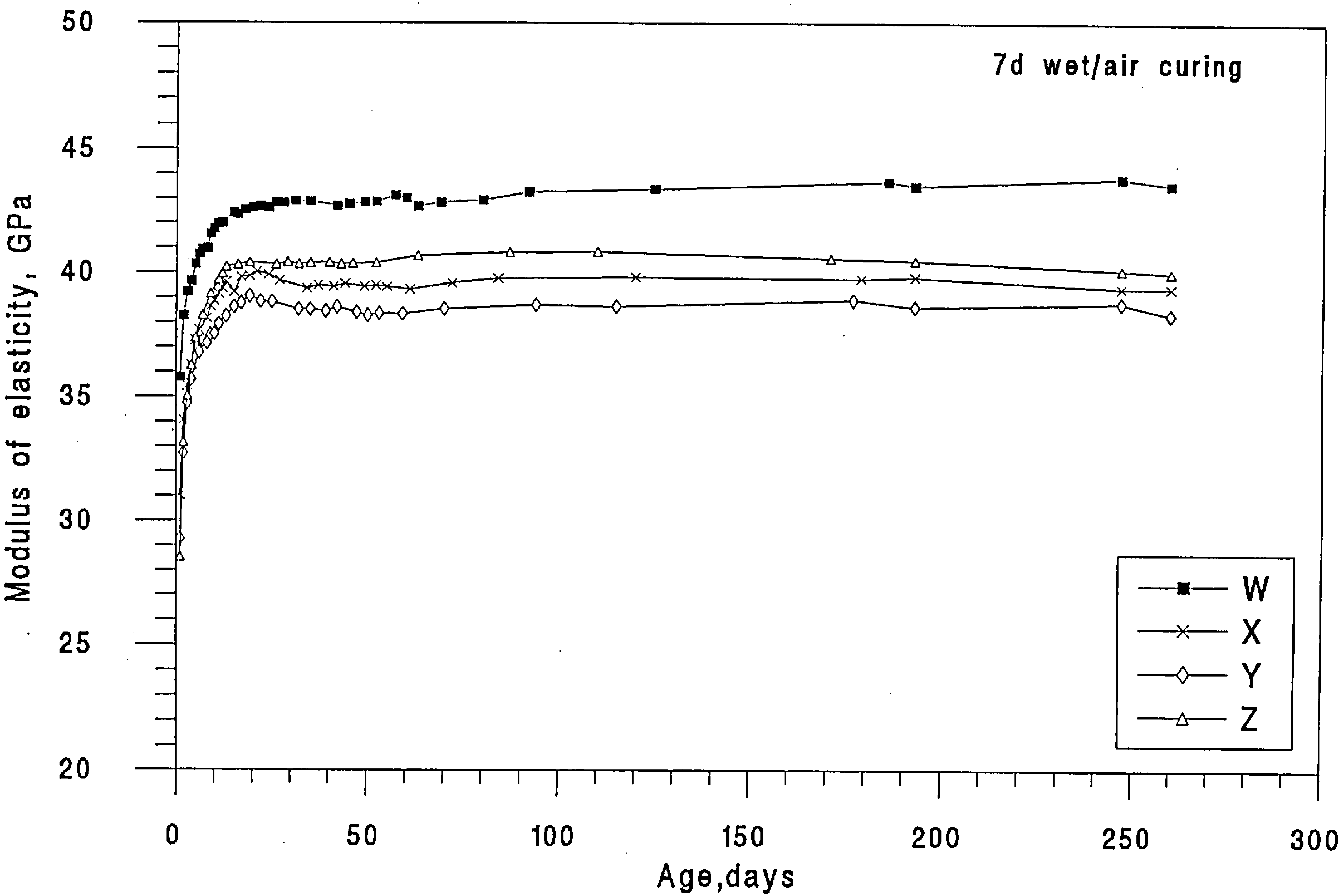


Figure 4.28 Effect of mineral admixtures on dynamic modulus for mixes W,X,Y and Z

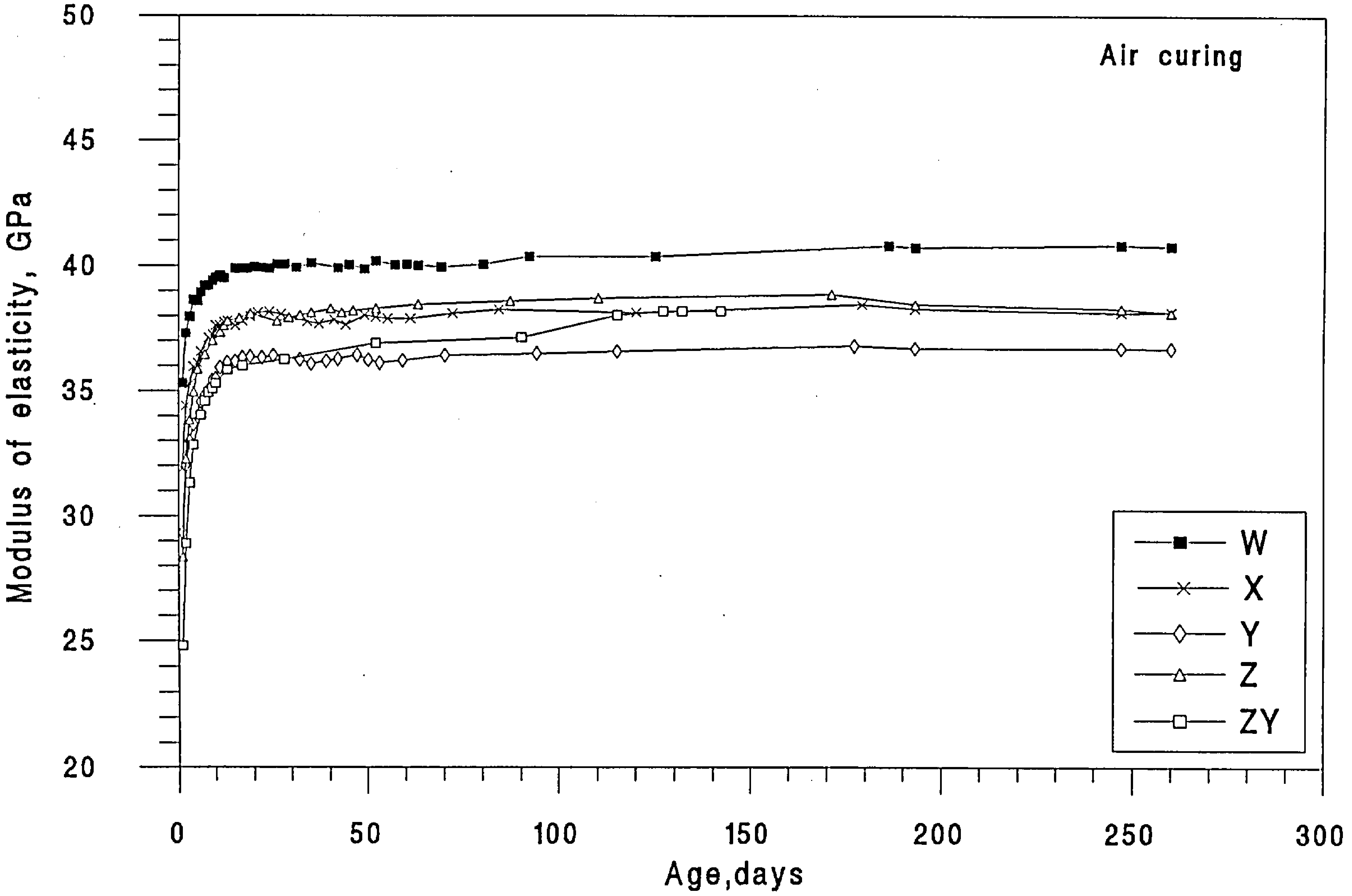


Figure 4.29 Effect of mineral admixtures on dynamic modulus for mixes W,X,Y,Z and ZY

slag replacement, the addition of 5,10 or 15% SF to the slag-cement concretes did not make a significant difference to the value of the elastic modulus at 28 days which remained at about 36GPa range. The mixture proportions of these concrete mixtures are shown in Table 4.11. However, there was some indication that the highest values were obtained for concrete containing 10% SF. Comparing with their results, far more higher compressive strengths and modulus values at 28 day age for all mixes were obtained in this study. In fact W and Z mix exhibited the same modulus values to the highest reported value (43GPa elastic modulus) published in literature carried out by Mehta [34], mix ZY modulus was even slightly higher, 44 GPa. From the results obtained here and data presented by other researchers it can be said that under wet curing conditions, there was no significant difference, if any, in elastic modulus between FA/SF and slag/SF or slag concretes and OPC concrete, and that elastic modulus do not increase significantly with increasing compressive strength of concrete.

Dynamic modulus development for mixes W, X, Y, Z, ZX and ZY are presented in Figure 4.28 for specimens under 7d wet/air curing conditions. The case was different for mix Z under this curing, where mix W showed higher values of modulus at all ages followed by mix Z and other mixes. The differences between control mix and other mixes were clearly pronounced and that the former modulus much less affected under this curing. Between 7 and 28 days there were no significant differences between the modulus of X, Z, ZX and ZY concretes, their modulus values increased gradually from 38 to 41 GPa whereas mix Y with 80 kg/m^3 FA exhibited slight lower modulus values in this period. This shows that modulus development in the first 28 days under 7d wet/air curing was not influenced by incorporation of 80kg/m^3 slag or 30kg/m^3 FA in concrete mixes, but with relative high FA content a reduction in the modulus was observed. However, the considerable contribution of slag or FA usually takes place after 2 to 3 weeks and thereafter their effects being more pronounced. At the age of 28 days, 5 to 10% loss in modulus was observed for all mixes compared to the control, the modulus values were 42.8, 39.7,. 38.6, 40.4, 41.06 and 40.1 GPa for mixes W, X, Y, ZX and ZY respectively. Beyond 28 days marginal improvement in modulus development was shown by mix W and a value of 43.6 GPa was obtained at 260 days age, whereas each one of the other mixes continued to exhibit the same values of dynamic modulus until later age although the values for Z mix were slightly higher than mix X, their values remained in the 40GPa range. In fact, at later ages mixes X, Y and Z showed somewhat marginal decrease in modulus values (pulse velocity data indicated similar signs of reduction).

Table 4.11 Mixture proportions [42]

Mix No.	Type of mixture*	W/(C+BFS)**	Relative proportions of cement and BFS, % by weight		Silica fume, % by wt of cement plus BFS	Batch quantities, kg/m^3					Superplasticizer L/m^3 of concrete
			Cement	BFS		Cement	BFS	Silica fume	F.A.	C.A.	
1	Reference	0.40	100	0	0	420	0	0	790	1055	—
2	Control		50	50	0	210	210	0	780	1060	—
3	5% Silica fume		50	50	5	210	210	21	750	1055	0.8
4	10%		50	50	10	210	210	42	725	1055	2.1
5	15%		50	50	15	210	210	63	700	1055	2.6
6	20%		50	50	20	210	210	84	675	1050	3.6
7	Reference	0.50	100	0	0	330	0	0	870	1050	—
8	Control		50	50	0	165	165	0	865	1060	—
9	5% Silica fume		50	50	5	165	165	17	845	1055	0.4
10	10%		50	50	10	165	165	33	825	1060	0.8
11	15%		50	50	15	165	165	50	805	1055	1.8
12	20%		50	50	20	165	165	66	785	1055	2.5
13	Reference	0.65	100	0	0	260	0	0	920	1050	—
14	Control		50	50	0	130	130	0	915	1060	—
15	5% Silica fume		50	50	5	130	130	13	900	1055	0.2
16	10%		50	50	10	130	130	26	880	1055	0.5
17	15%		50	50	15	130	130	39	870	1055	1.2
18	20%		50	50	20	130	130	52	850	1055	1.6

* Reference mixture: 100% normal portland cement
Control mixture: 50% normal portland cement plus 50% BFS
Silica fume mixture: 50% normal portland cement plus 50% BFS plus additions of silica fume
**Water/(cement + BFS) by weight

Another important point which can reveal some interesting engineering implications can be, however, drawn from the results shown in Table 4.10. At 28 days, 7d wet/air-cured concretes had slightly higher compressive strength than concretes continuously cured in water; yet the former showed a loss in modulus of some 6% compared to the latter. Similar trends were reported by Swamy [19], for concretes of 50MPa (28d) having 50 and 65% by weight cement replacements with slag. However, in his work the loss in modulus was higher than that observed here. He attributed the loss in elastic modulus to internal microcracking. This phenomenon was also observed at 90 and 260 days. Both FA/SF and slag/SF concretes cured under the same two curing conditions exhibited a strength increase of 10 to 20% from 28 days to 90 days and 25% from 28 to 260 days, and yet registered an approximately 10 and 15% decrease in dynamic modulus from that at 28 days, respectively. On the other hand the control mix with the same increases in strength as above under similar curing conditions, indicated about 5% loss in dynamic modulus at 90 and 260 days. Similar losses have been reported by other researchers[19].

The dynamic modulus development under air curing condition for mixes W, X, Y, Z and ZY shown in Figure 4.29 appears to follow similar trends to those in Figure 4.28 but with lower modulus values. Like under 7d wet/air curing condition the control mix showed the highest modulus values at all ages while the 80 kg/m^3 FA mix (Y) showed the lowest modulus. Between 7 and 28 days there was little change in modulus of mix W whereas the change in other mixes still remained considerable. At this period, however, there were no significant differences between the modulus of X, Z and ZX mixes, mixes Y and ZY exhibited lower modulus values but they were close to each other compared with wet-cured concretes; air drying with no water curing produced significant reductions in dynamic modulus, 6% for control mix and 10% for other mixes, within 28 days, respectively, also the modulus values after 28 days did not continue to increase with increasing compressive strength. Very little change in modulus between 28 and 260 days was observed for mix W. The modulus values at 28 days were 40.1, 38.1, 36.3, 37.9, 37.7 and 36.2 GPa for mixes W, X, Y, Z, ZX and ZY respectively. At 90 days the modulus of the X concrete approached the value reached by the Z concrete; at 260 days the modulus of the former concrete was the same as of the latter concrete which showed marginal decrease in modulus at this age. This reduction was also pronounced in pulse velocity as shown later. Similar phenomena was reported by Swamy [19], with continued air drying to 6 months, there was little change in the elastic modulus, although there was a discernible indication of loss in elastic modulus with prolonged dry storage. The dynamic modulus ranged from a low of 36.6 GPa for Y mix to a high of 40.8 GPa for control mix at 260 days. Prolonged drying can thus create adverse internal microcracking not readily indicated by compressive strength values [19].

However, from the result analysis of the considered mixes under 7d wet/air and air curing conditions two facts become apparent; one was that the modulus of control mix containing no mineral admixtures showed better higher values than the other mixes; and that incorporation of 30 kg/m^3 FA and both 80 and 165 kg/m^3 slag retarded the dynamic modulus to some extent but with relative higher of FA (80 kg/m^3) incorporation further reduction in modulus was observed i.e. the modulus is more sensitive to the incorporation of FA than slag. The other interesting finding was to note that the results for the FA/SF and slag/SF concretes showed no modulus development between 28 day and 260 days, with an indication of loss in modulus with prolonged dry curing. This enables the prediction of the late age dynamic modulus.

4.5.3 Relationship between dynamic modulus and compressive strength

In order to relate the dynamic modulus of elasticity of concrete, Ed, to its compressive strength, fcu, statistical analysis was carried out using the following model widely used by researchers:

$$E_d = af_{cu}^b \text{, where a and b are constants}$$

The values for different concrete mixes under wet, 7d wet/air- and air-cured conditions are depicted in the scatter diagram in Figure 4.30. Each value corresponds to the average of two measurements.

The degree of association or strength of relationship between two variables is represented by the correlation coefficient; and it can be seen from the correlation coefficients presented in the figure that there is a high correlation between each curing condition for dynamic modulus and its compressive strength of all mixes. However, the figure confirms a number of points discussed earlier for concrete mixes cured under different curing regimes :

1. The highest correlation was found in wet cured specimens whereas air cured specimens showed relatively poor correlation almost similar to the 7d wet/air- cured specimens where their scatter of results was somewhat greater than for wet-cured ones.

2. The relationship between modulus and strength under 7d wet/air curing was about the same to that under air curing conditions, the modulus values that could be obtained would be nearly the same.

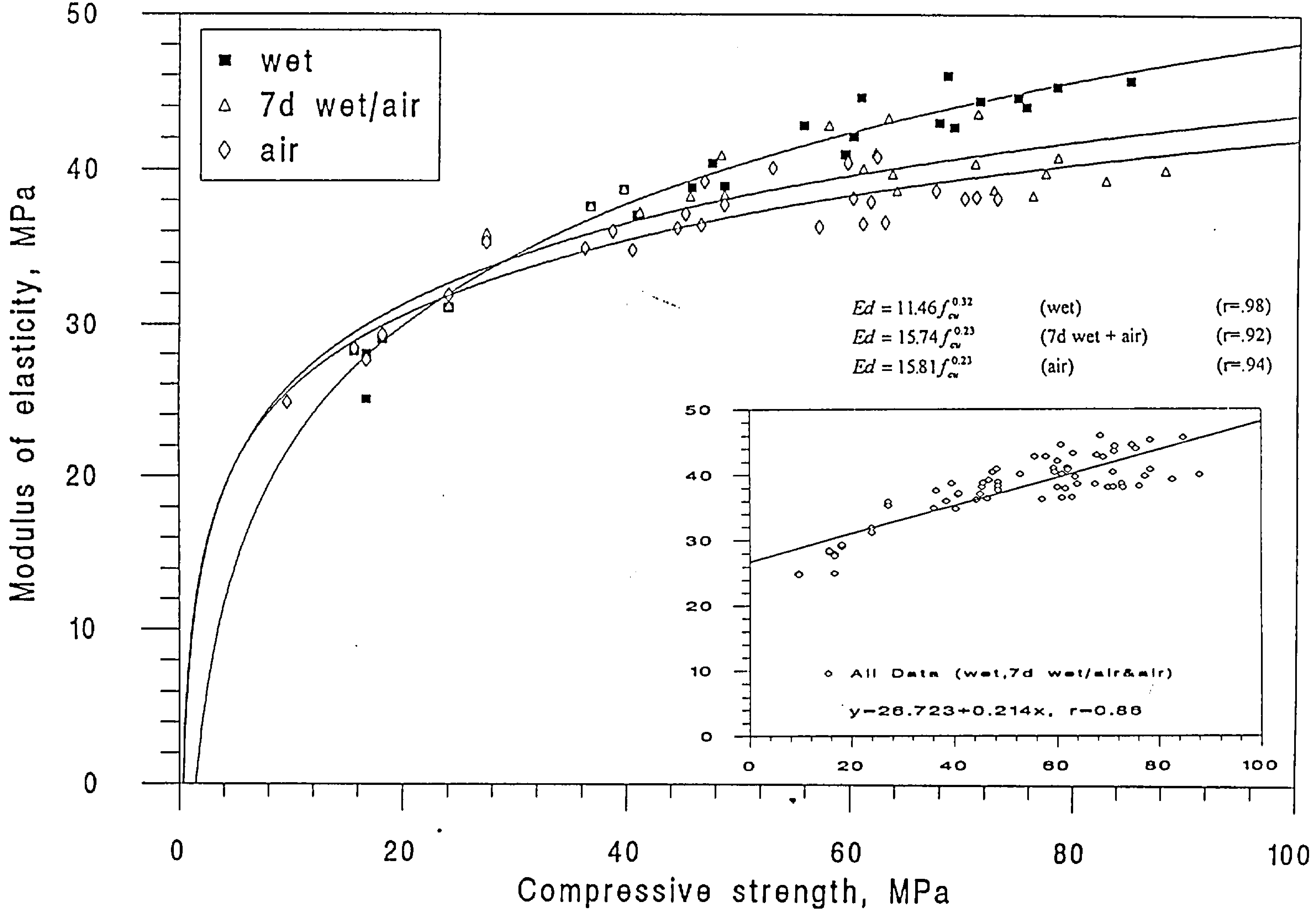


Figure 4.30 Relationship between dynamic modulus and compressive strength

3. There is no significant difference in dynamic modulus under wet, 7d wet/air and air-cured specimens at a strength level of about 30MPa.

4. The differences in modulus between wet and both 7d wet/air- and air-cured specimens increases as the compressive strength increases, differences of about 6GPa was observed at 260 days. The differences reflect the adverse effect of air curing and the 7 day wet/air curing seems to have limited beneficial effects on modulus development.

In general the results shown in Figure 4.30 confirm the better performance of wet cured specimens and that the most important influence on changes of dynamic modulus is continuous water curing; besides, the changes in modulus under different curing conditions at early ages were not significant. The dynamic modulus does not parallel the compressive strength development with increasing age; for concrete cured wet, the compressive strength increases with age but, as previously observed, any increase in modulus is very small; concretes cured in air or 7d wet/air from the age of 28 days show no change in modulus.

The following satisfactory regression equations were obtained from the analysis of the data in relating dynamic modulus and modified compressive strength.

$$Ed = 11.46 f_{cu}^{0.32} \qquad \text{(wet)} \qquad (r=.98)\,(1)$$
$$Ed = 15.74 f_{cu}^{0.23} \qquad \text{(7d wet + air)} \qquad (r=.92)\,(2)$$
$$Ed = 15.81 f_{cu}^{0.23} \qquad \text{(air)} \qquad (r=.94)\,(3)$$

A comparison of the dynamic modulus obtained in this study for all wet cured mixes at 20°C is made in Figure 4.31 with those recommended by BS8110:Part 2:1985[17,92] for concrete in structural use as well as with other available data [55,93]. The equations are presented in the same figure. The results show that values predicted by equation (1) showed lower modulus than that given by BS8110 at compressive strength values below 55MPa (about 28 d strength of all mixes) whereas beyond this strength level the code values appears to be somewhat lower than the values obtained. This figure also shows that dynamic modulus of elasticity is higher for the mixes investigated in [55] and the differences in both cases increases as the compressive strength increases. The use of SF plus FA or slag appears to enhance the dynamic modulus. On the other hand equation (1) was similar in shape to that found in reference [93], the results obtained show about 12% lower modulus.

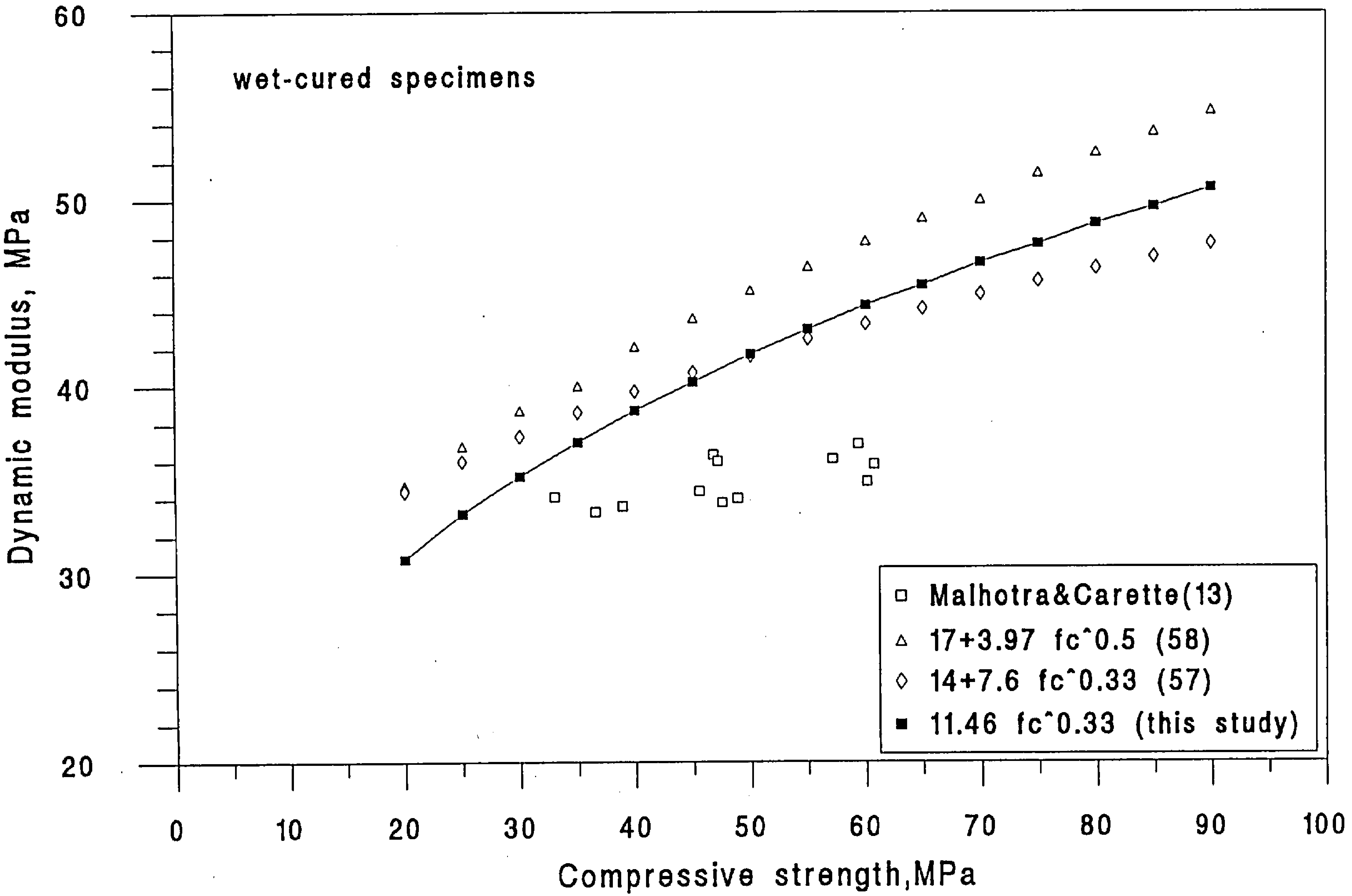


Figure 4.31 Relationship between dynamic modulus and compressive strength

4.6 Ultrasonic Pulse Velocity

4.6.1 Effect of curing

Ultrasonic pulse velocity in concrete is influenced by many factors of particular significance are the proportions of the mixture, age, curing condition, moisture content of the concrete, presence of reinforcement and temperature. Because of the complex interaction of these factors, however, the pulse velocity cannot be used as a direct indicator of compressive strength [3]. Table 4.12 shows the pulse velocity values obtained from concrete prisms of control and FA/SF and slag/SF concretes at various ages and when subjected to wet, 7d wet/air and air curing conditions. Figure 4.32 to 4.36 show the effect of the above curing conditions on each of the six mixes investigated in this study. The time taken by the pulse to travel through the concrete was measured with an accuracy of ± 0.1 microsecond.

Figure 4.32 shows the pulse velocity variations for control mix under wet, 7d wet/air and air curing conditions. The wet-cured specimens exhibited the highest pulse velocity values. Between 1 and 28 days there were no significant differences between the three curing conditions pulse velocity values, the one day values were 90% of the 28 days pulse velocity which was about 4.6 km/s for all different cured specimens. Beyond 28 days there was marginal increase in both 7d wet/air- and air-cured specimens up to 90 day age and after which signs of reduction in pulse velocity were observed, while the wet-cured specimens continued to show development in pulse velocity up to 260 days. At this age the pulse velocity of wet-cured specimens was about 5% higher than those for the other two curing condition specimens; the pulse velocity values was 4.72, 4.60 and 4.50 km/s for wet, 7d wet/air- and air-cured specimens respectively. Although from the results it appears that control mix pulse velocity values were not much affected by the curing conditions, but distinct enough to reflect the effect of curing and hence the internal microstructure.

The effect of wet, 7d wet/air and air curing conditions on X and Y FA/SF mixes are presented in Figure 4.33 and 4.34, the trend in pulse velocity for different curing conditions is similar to the trends obtained for control mix. The wet-cured specimens of both mixes yielded the highest pulse velocity values compared with 7d wet/air- and air-cured specimens respectively. For mix X the pulse velocity of the three curing conditions were very close for the period of 1 to 28 days; whereas for mix Y the pulse velocity differences between the different cured specimens appeared after 7 days and were somewhat considerable at the age of 28 days. This was attributed to the relative

Table 4.12 Pulse velocity in mineral admixture prisms under various curing conditions, km/s

Curing condition	Mixes Age, day	W	X	Y	Z	ZX	ZY
Wet curing	1	4.20	4.05	3.95	3.90	-	3.71
	7	4.46	4.42	4.40	4.45	-	4.42
	28	4.58	4.57	4.58	4.45	-	4.69
	90	4.66	4.64	4.63	4.67	-	4.73
	260	4.72	4.68	4.66	4.71	-	-
7d wet / air curing	1	4.20	4.05	3.96	3.90	3.81	3.68
	7	4.50	4.41	4.40	4.45	4.43	4.39
	28	4.6	4.53	4.50	4.61	4.59	4.57
	90	4.6	4.44	4.50	4.63	-	-
	260	4.6	4.46	4.45	4.51	-	-
Air curing	1	4.22	4.09	3.97	3.90	3.83	3.67
	7	4.46	4.36	4.26	4.33	4.28	4.20
	28	4.55	4.49	4.41	4.51	4.46	4.39
	90	4.54	4.50	4.41	4.54	-	4.43
	260	4.50	4.39	4.35	4.42	-	-

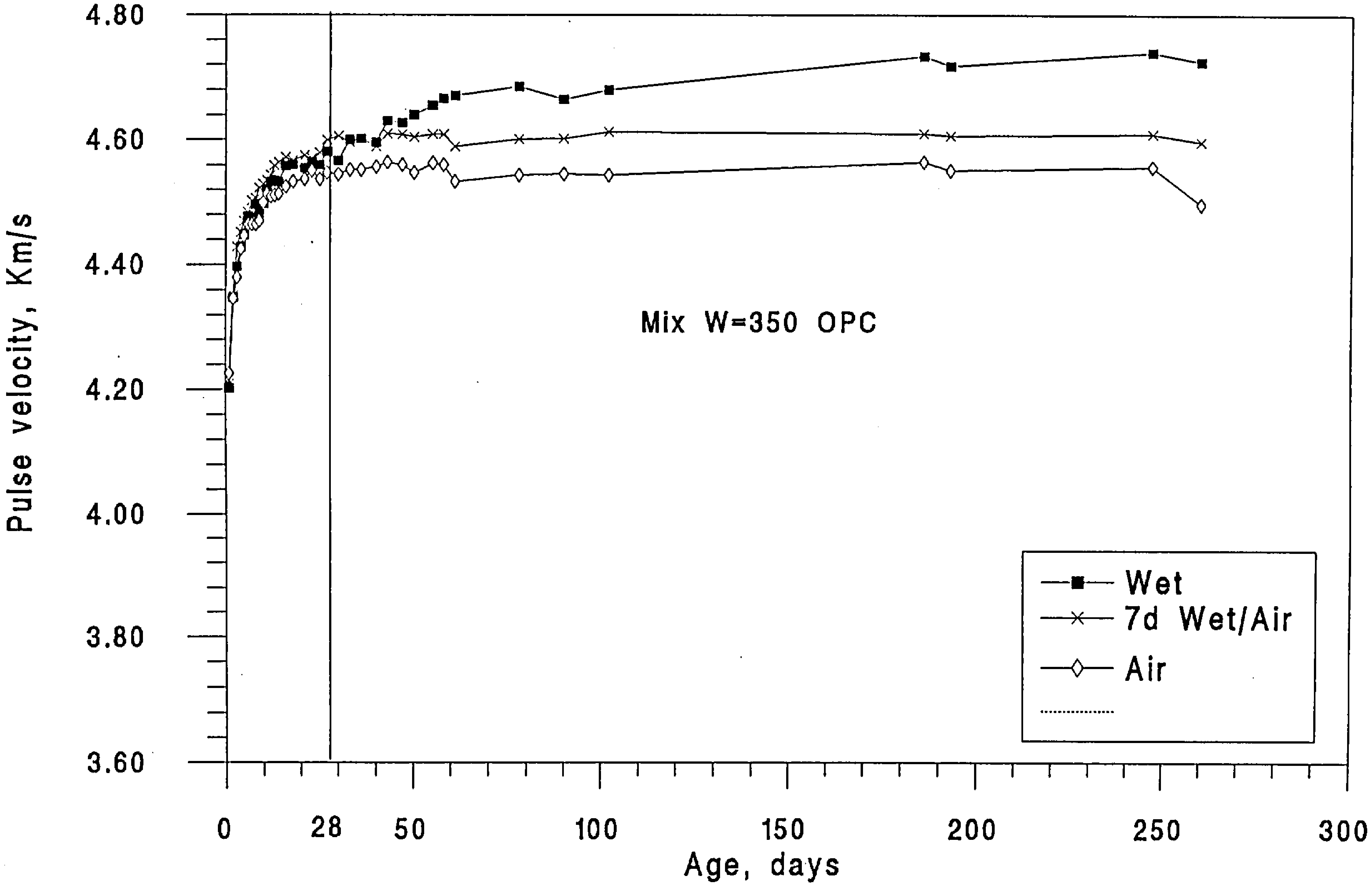


Figure 4.32 Effect of curing on pulse velocity for control mix W

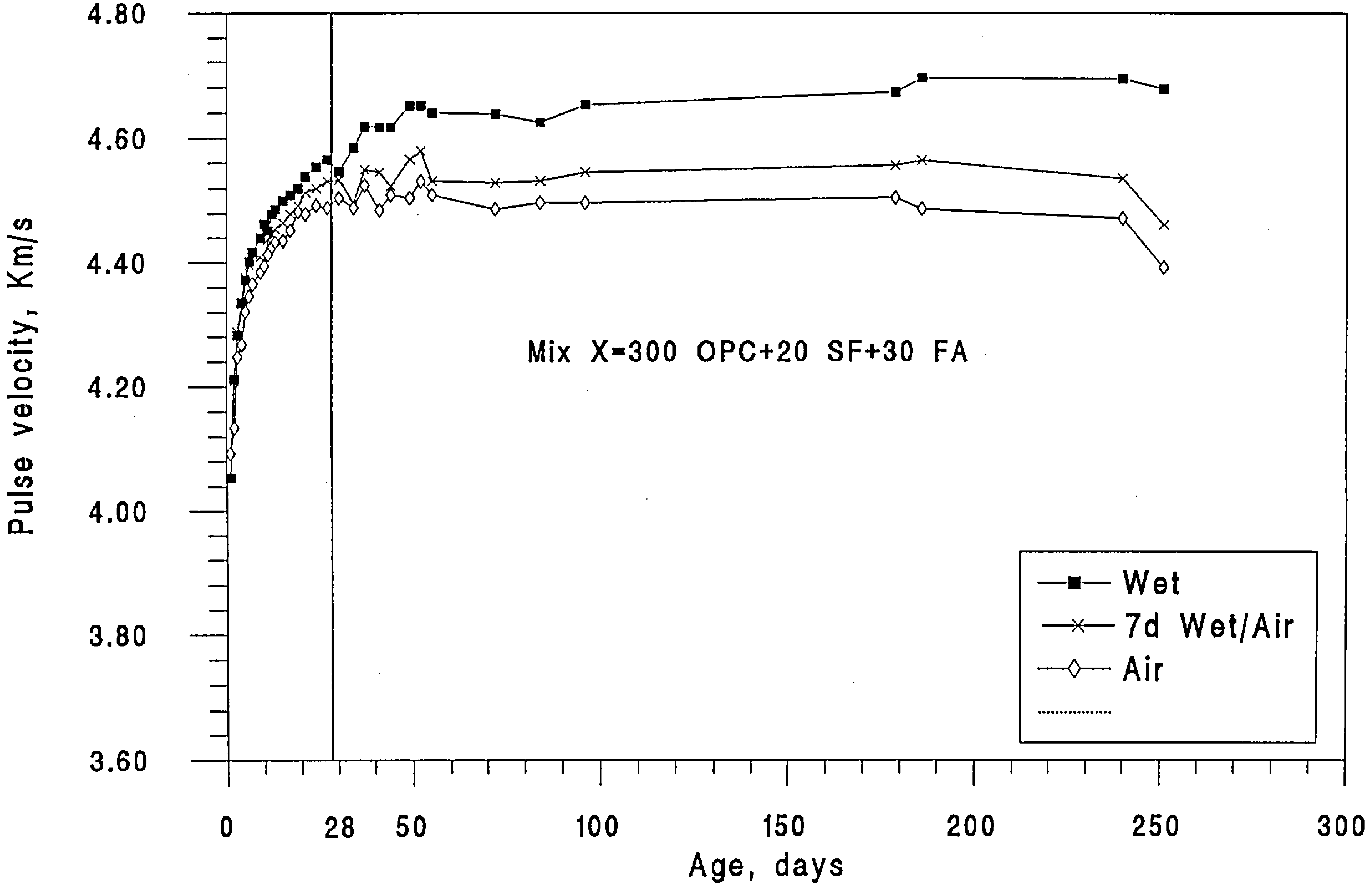


Figure 4.33 Effect of curing on pulse velocity for mix X

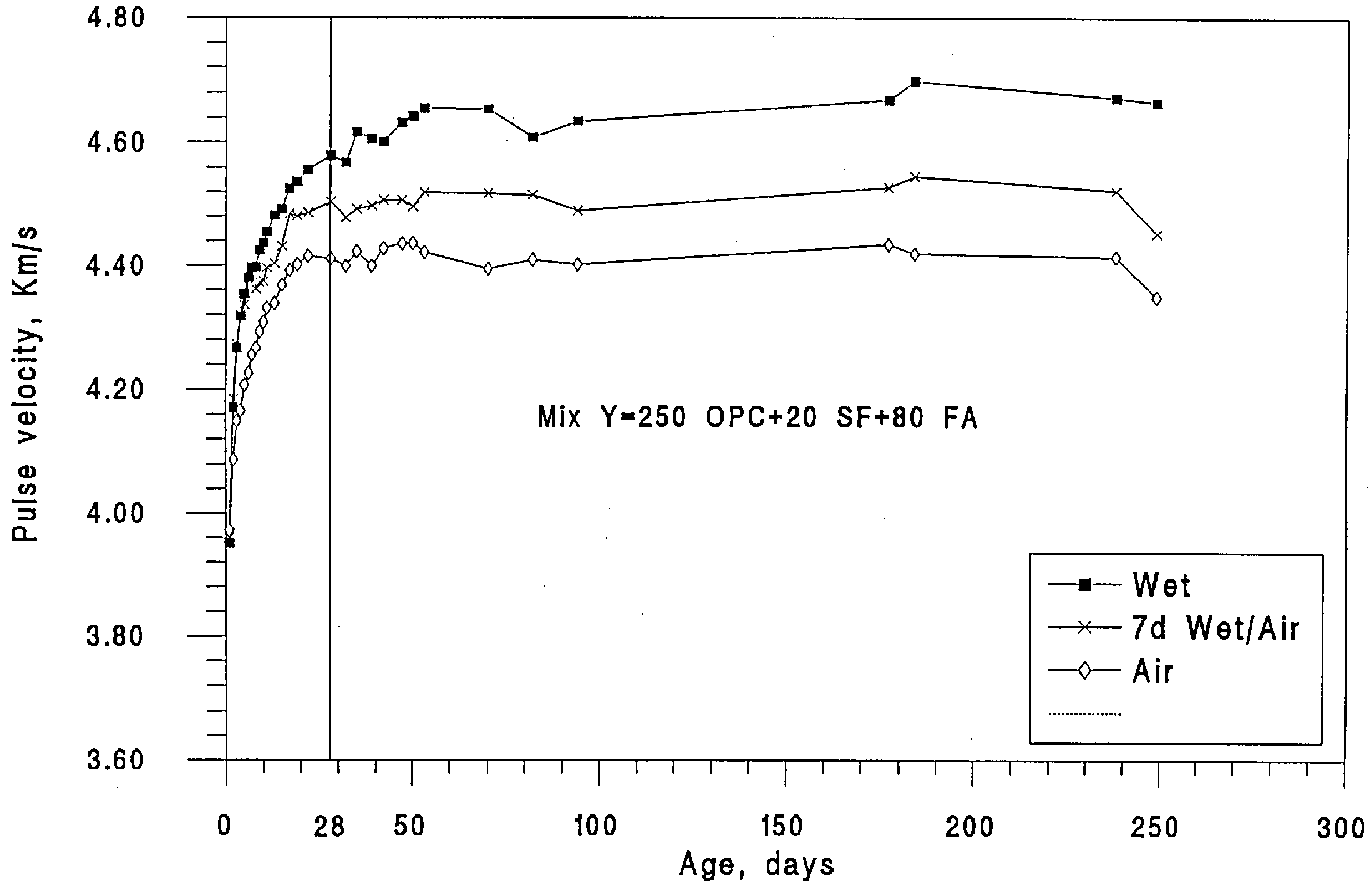


Figure 4.34 Effect of curing on pulse velocity for mix Y

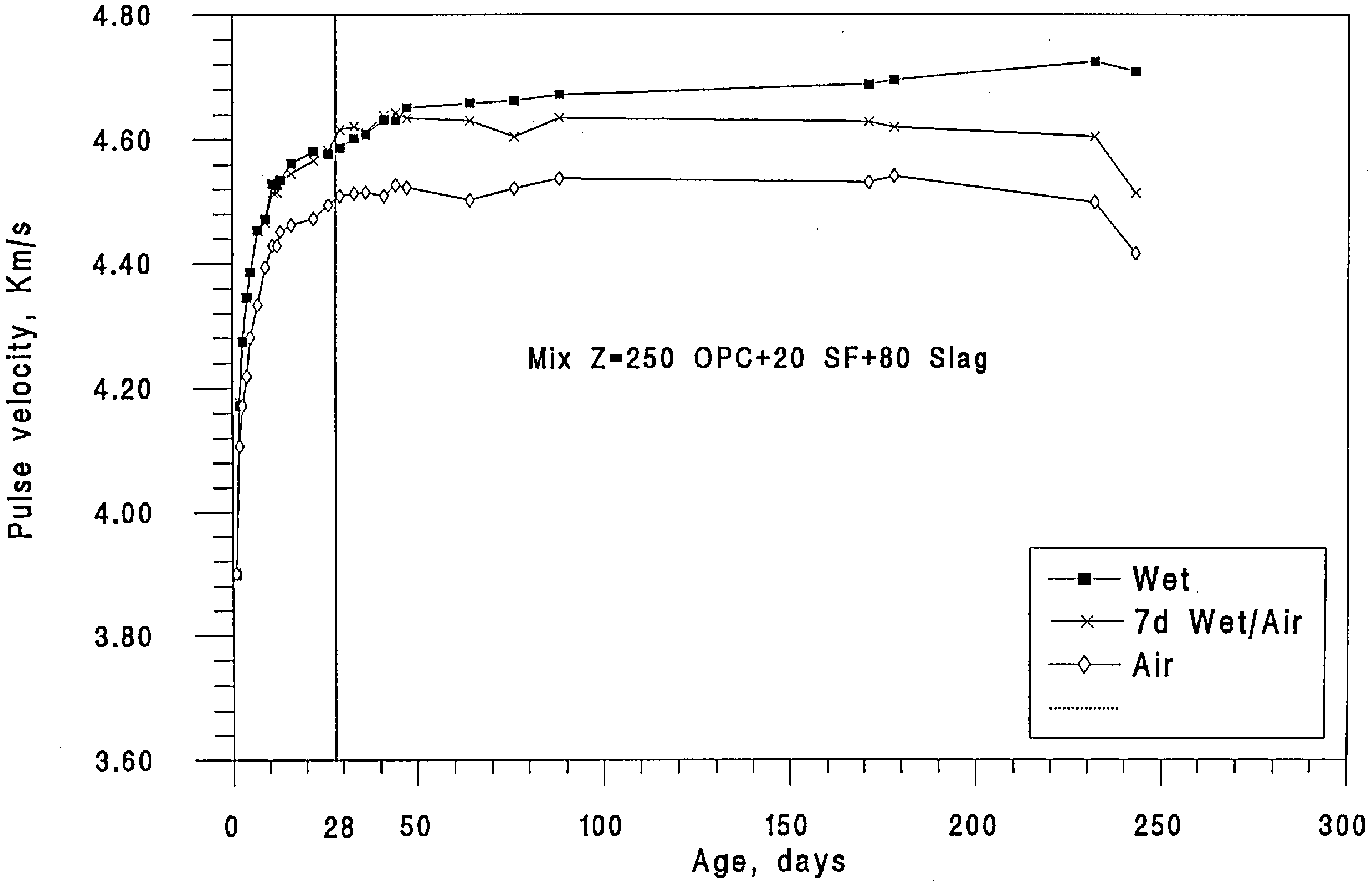


Figure 4.35 Effect of curing on pulse velocity for mix Z

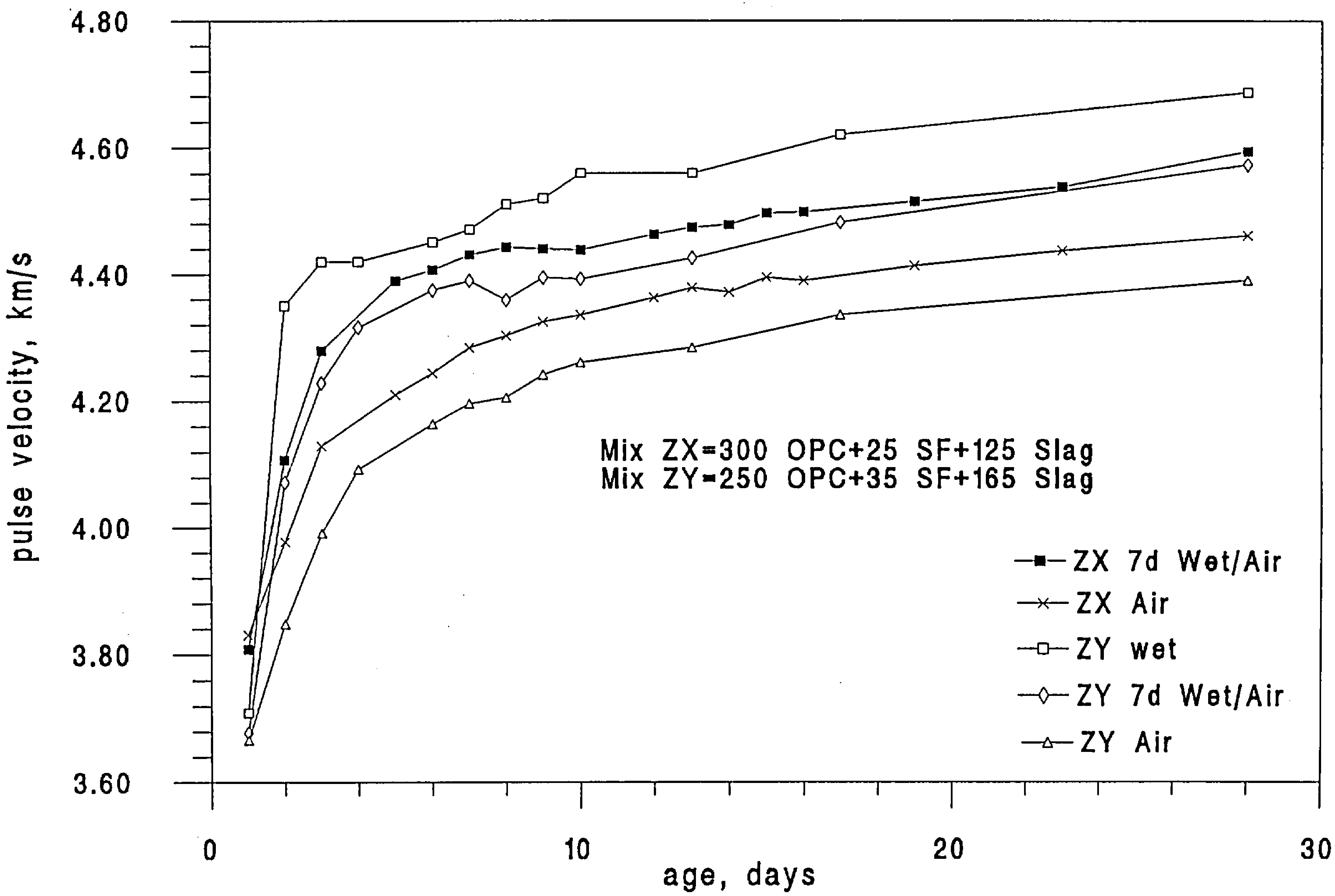


Figure 4.36 Effect of curing on Pulse velocity for mixes ZX and ZY

high FA incorporation (about 30% of total binder content compared to about 10% for mix X) in mix Y. The pulse velocity of wet-cured specimens of mix Y were about 5% higher than the air cured specimens at the age of 28 days, similarly the compressive strength of wet cured specimens was higher by the same amount than the air-cured ones. The differences in pulse velocity values at the age of 28 days between the wet- and 7d wet/air-cured specimens of this mix were marginal. This shows the bad effect of air-curing compared to the 7d wet/air curing advantage which brought pulse velocity values to a level comparable with wet-cured ones. With 7d wet/air and air curing to 90 days, there was little change in the pulse velocity at 260 days (about 0.1 km/s) (Figure 4.33 & 4.34). On the other hand the wet-cured specimens pulse velocity continued to increase up to 260 days and gave a similar value for both mixes at this age, 4.68 and 4.66 km/s for mixes X and Y respectively, where they were higher by 5 and 7% than 7d wet/air- and air-cured specimens respectively. As a result it can be said that the effect of each curing condition on pulse velocity development of both mixes was similar and that the air cured specimens pulse velocity was more affected than the pulse velocity of 7d wet/air-cured ones.

The influence of various curing regimes on the pulse velocity development for mixes Z, ZX and ZY are shown in Figures 4.35 and 4.36. From the pulse velocity values given in Table 4.12 and trends shown in these two figures it can be said that there were no significant differences between the wet- and 7d wet/air-cured specimens of the slag/SF concrete mixes for the period of 1 to 28 days, although by very close inspection of the graphs and readings it appears that the 7d wet/air cured specimens of mix Z performed better (i.e. less affected) followed by mix ZX and then mix ZY when compared to each other. This is in fact expected, because the higher the slag content (ZY>ZX>Z) the more wet curing (moisture) is needed for the hydration process to take place and that 7 day wet curing might not be enough for high content slag concrete. The pulse velocity values for the three mixes under wet and 7d wet/air curing condition at the age of 7 days were the same about 4.45km/s as well as at the age of 28 days about 4.6 km/s. On the other hand, the effect of air curing on pulse velocity of the three mixes was clearly seen. For example, at the age of 28 days, mix Z exhibited a pulse velocity of 4.6 km/s which was the largest at this age followed by 4.46 and 4.39 km/s for ZX and ZY air-cured specimens respectively. In other words, mix ZY was the most badly affected by air curing followed by mix ZX and then mix Z, which was the least affected. In fact the effect of air curing on compressive strength, flexural strength and dynamic modulus followed the same order in the three mixes. However, it is noteworthy to know that the pulse velocity of 7 dwet/air-cured specimens of the three mixes were slightly higher than air cured specimens at 7 and 28 days age, the difference might not be significant but it reflected the effect of curing that took place on the internal microstructure of these concretes. Between 28 and 90 days there was a slight increase in pulse velocity of 7d wet/air- and air-cured specimens for mix Z; after 90 days similar to mixes X and Y no increase in pulse velocity of these specimens was observed although a slight loss in pulse velocity with both curing conditions was there at 260 days. On the other hand, the wet-cured specimens continued to show higher pulse velocity values to 260 day and were 5 and 7% higher than 7d wet/air- and air-cured specimens at this age respectively.

As far as the influence of curing conditions on pulse velocity the following observations can be made:

- The wet-cured specimens of all mixes yielded the highest pulse velocity values followed by 7d wet/air cured specimens and then the air cured ones.

- The effect of curing regimes on pulse velocity is similar to that on dynamic modulus of elasticity.

- For each mix the 1 and 28 days values of pulse velocity were very similar for the three curing conditions, i.e. the effect of curing regimes being more pronounced at 28 days and beyond.

- Control and FA/SF and slag/SF concretes performed similarly in the wet curing condition, whilst under the worst conditions of curing the 80 kg/m^3 SF/FA concrete recorded lower pulse velocities at all ages.

- At 260 days all moist cured mixes were 5 and 7% higher than 7d wet/air and air cured ones.

- 7d wet/air- and air-cured concretes showed slight reduction in pulse velocity at 260 days compared with continued pulse velocity development for wet-cured concretes.

- Finally, however, the results suggest that ultrasonic pulse velocity measurements could be used on site to monitor curing efficiency quickly and non-destructively particularly in the first few weeks, and that if FA/SF and slag/SF concretes were not properly cured and allowed to continued exposure to a drying environment (air curing), its strength and durability related properties would be seriously impaired.

4.6.2 Effect of cement replacement materials

The effect of cement replacement materials on the development of Ultrasonic pulse velocity of control, FA/SF and slag/SF concrete under wet, 7d wet/air and air curing conditions were shown in Figures 4.37 to 4.39.

Pulse Velocity at 1 and 7 days

Since both dynamic modulus and pulse velocity are theoretically interrelated, the development in pulse velocity for all mixes, regardless of the curing condition, was in general similar in behaviour to that of dynamic modulus. The increase in pulse velocity values between 1 and 7 days occurred at a rapid rate, and at 7 days the increase was about 97% of that at 28 days for all mixes under different curing conditions. For slag/SF mixes (Z, ZX and ZY) the increase between 1 and 7 days varied from 14 to 20% whereas this increaseforFA/SF mixes was about 10%, and about 6% the lowest for control mix. The results confirm clearly the observation made earlier concerning compressive strength and dynamic modulus behaviour for different mixes at this age, although the magnitude of their changes were different. This rapid increase is explained by the early role played by SF and related to internal structure of each mix. However, the pulse velocity of control mix was the highest at one day age, 4.2 km/s, compared with 4.05, 3.95, 3.9, 2.8 and 3.68 km/s for mixes X, Y, Z, ZX and ZY respectively. The 7 day pulse velocity values of different mineral admixture mixes under wet and 7d wet/air curing conditions were found to be equal or very slightly less than the control mix value. Whilst under air curing conditions the differences in pulse velocity values were somewhat considerable, the control mix exhibited the highest value of 4.46 km/s, about 5% higher than the other mixes. Pulse velocity of mixes X and Z were close, as well mixes ZX and Y, mix ZY obtained the lowest pulse velocity values as expected. The increase after 7 days was gradual, and the increase between 7 and 28 days was 3% for all mixes under different curing regimes.

Pulse Velocity at 28 days and beyond

The data in Table 4.12 and Figure 4.37 show that under continued wet curing, concretes at all replacement levels showed increasing pulse velocity, reflecting the increase in compressive strength and dynamic modulus, as well as the development of a dense internal structure.

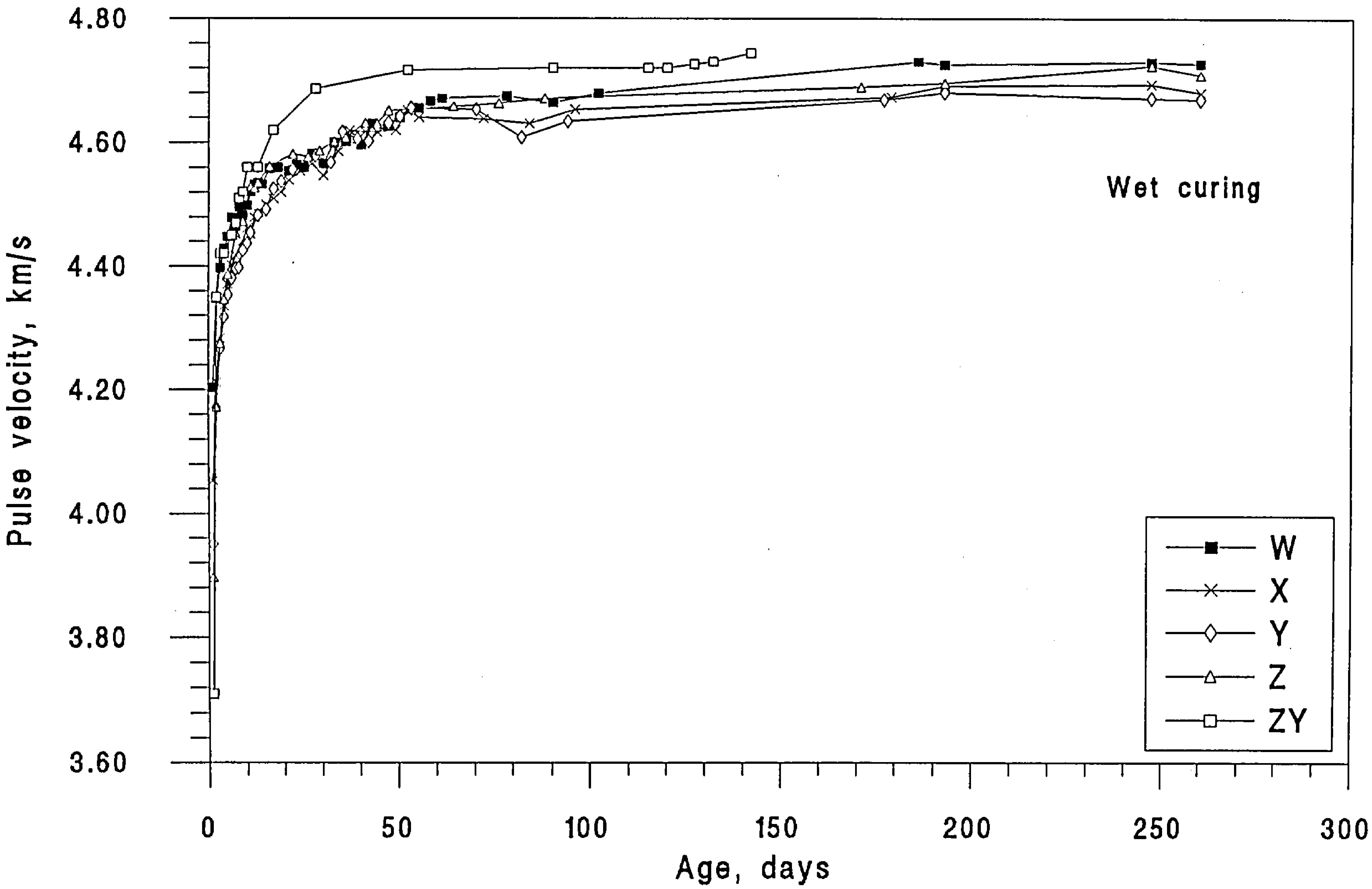


Figure 4.37 Effect of mineral admixtures on pulse velocity for mixes W,X,Y,Z and ZY

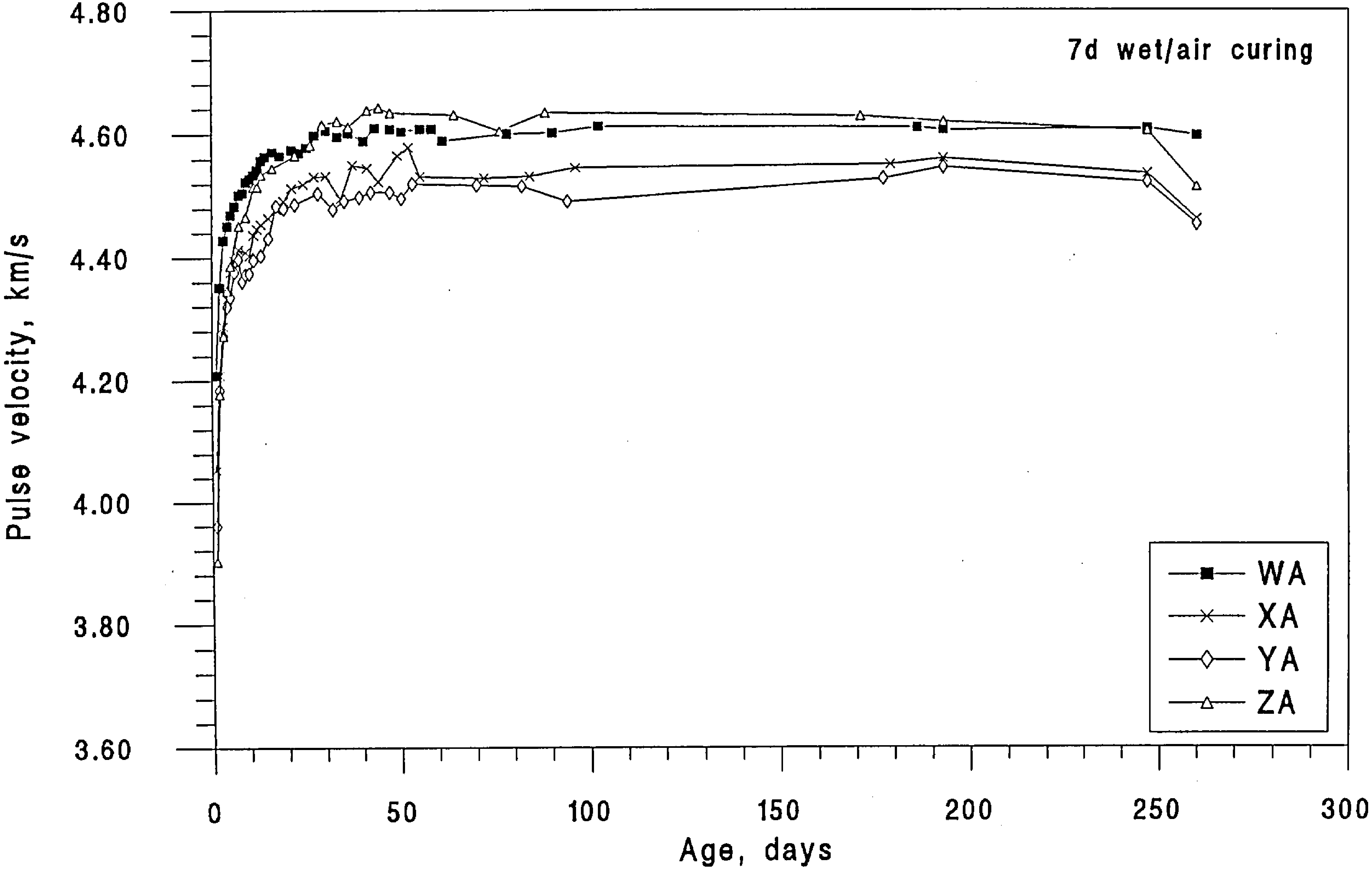


Figure 4.38 Effect of mineral admixtures on pulse velocity for mixes W,X,Y and Z

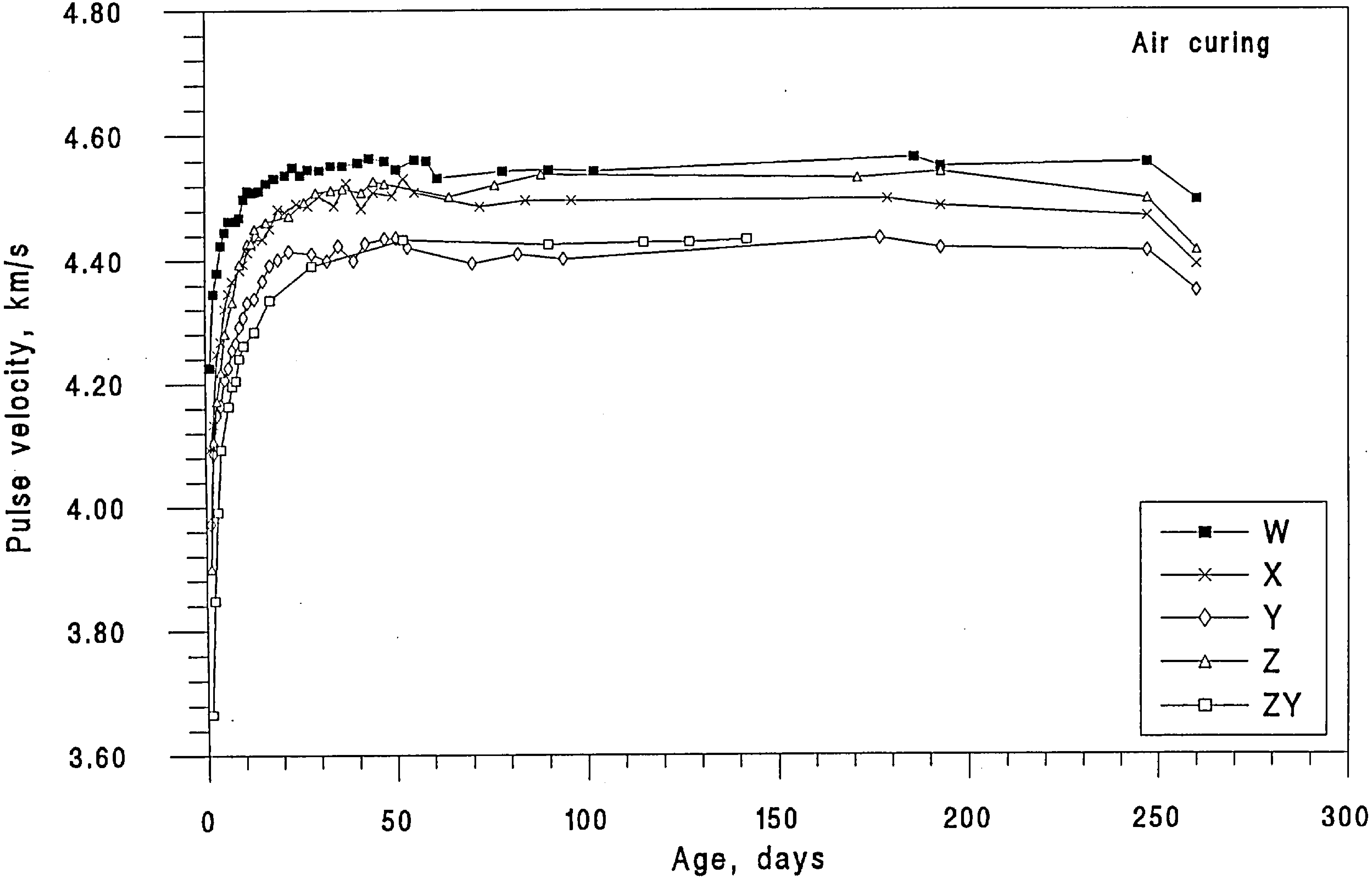


Figure 4.39 Effect of mineral admixtures on pulse velocity for mixes W,X,Y,Z and ZY

By comparing the pulse velocity values of different mixes at each age, it appeared that there were no significant differences and that the presence of the mineral admixtures seems dose not alter the pulse velocity development, although it seemed that mix Y pulse velocity was slightly lower than other mixes at later ages. The pulse velocity values for all mixes were about 4.58, 4.66km/s at 28 and 90 days respectively, and remained in the 4.72 km/s range at 260 days. The above results were found to be consistent with dynamic modulus development under wet curing conditions of concrete containing mineral admixtures. But in regard to the compressive strength for the corresponding mixes and curing conditions it varied quite widely, which means that pulse velocity should not be used as a general indicator for compressive strength.

In Figure 4.38 the variations of pulse velocity with time under 7d wet/air curing condition for the different concrete mixes were shown. The figure shows that pulse velocity in the slag/SF mix (Z) was a bit lower than control mix (W) until about 28 days, and then it became higher throughout and indeed showed loss in pulse velocity at 260 days. Similar behaviour in compressive strength development was shown by mix Z but its strength continued to increase and exhibited the largest value at 260 days compared to all other mixes, whereas its dynamic modulus was somehow lower than the control mix at all ages, and this might show that the modulus is somewhat more sensitive to the effect of 7d wet/air curing than the compressive strength. In regard to ZX and ZY mixes, at 125 and 165 kg/m^3 cement replacement with slag in concrete mixture, proportioned to have 50MPa compressive strength at 28 days, it was found that the initial pulse velocity values for these two concretes were lower than the control concrete; this is due to the fact that the slag proportion was higher and could not contribute as a binder until at a later age whereas SF did its job in boosting the strength and other properties at early ages.

However at 28 days both slag/SF mixes (ZX and ZY) pulse velocity values were comparable to that of the control and Z concretes. The pulse velocity values at 28 days age were 4.6, 4.61, 4.59 and 4.57 km/s for mixes W, Z, ZX and ZY respectively. At 90 days the pulse velocity values were 4.6 and 4.63km/s for the control and Z mixes, respectively. On the other hand mixes X and Y, at 30 and 80 kg/m^3 cement replacement with FA in concrete mixture, exhibited lower pulse velocity values than the control and other slag mixes at all ages. There was no significant difference between X and Y mixes, although by close inspection of the figures it appeared that pulse velocity values of mix X were slightly higher than mix Y ones. Similar behaviour was also observed when dynamic modulus was considered for mixes X and Y which is presented in Figure 4.28 the differences were more clear there. It thus appears that incorporation of FA, even with small amount, decreases the pulse velocity of concrete mixes and with high replacement levels of FA similar to that of slag content in mixes ZX and ZY further reduction in pulse velocity would be obtained as well as other properties, which mean that incorporation of slag in concrete mixes is advantageous and results in better denser structure. The pulse velocity values at 28 and 90 days were the same for each mix 4.54 and 4.50 km/s for mixes X and Y respectively.

Figure 4.39 compares the pulse velocity in air curing conditions for the plain different mineral admixture concretes. It shows that the pulse velocity in the control mix was higher than the velocities in the other mixes, but same to that in mix Z at 90 days. The velocities in mixes X and Z were about the same and greater than that in ZX, ZY and Y mixes for the period (1 to 28 days). The pulse velocity values at 28 days were 4.55, 4.49, 4.41, 4.51, 4.46 and 4.39 km/s for mixes W, X, Y, Z, ZX and ZY respectively. Further the pulse velocity in all mixes, similar to dynamic modulus values, did not show any considerable development, and pulse velocity losses in all mixes were obtained at 260 days. However, from the figure it seems that concrete made with FA/SF is more susceptible to drying conditions than concrete made with slag/SF, this is clearly seen with mix Y where cement replacement level by FA and SF was the same as that of mix Z even though it exhibited much lower pulse velocity values than mix Z. The same trend was also obtained when compressive and flexural strength as well as dynamic modulus values were considered and similar conclusions were reached for mix Y.

In general pulse velocities of concretes cured in air (laboratory) and concretes given 7 day wet curing followed by air curing increased with age until 28 days, after which all the pulse velocity readings remained unchanged and at 260 days showed slight loss in pulse velocity (2% of that at 28 days) (Figure 4.38 and 4.39), while compressive strength showed continued increase up to 260 days (Table 4.2). On the other hand, flexural strengths and dynamic modulus also showed loss at 260 days for the air and 7d wet/air curing regimes (Table 4.7 and 4.9). Loss of flexural strength and dynamic modulus are an indication of internal microcracking, which is readily picked up by changes in pulse velocity [19]. Swamy [19] reported pulse velocity and flexural strength losses for the drying and 7d wet and drying regimes, the concretes having 50 and 65% cement replacement with slag. However, the pulse velocity measurement indicated the beginning of internal microcracking in FA/SF and slag/SF concretes with or without initial 7d wet curing, and continued exposure to a drying (air curing) can thus have resultant adverse consequences on the long term durability of such concretes. Moreover, both pulse velocities and dynamic modulus measurement techniques offer potentially nondestructive test methods to identify the physical condition and quality of concrete structures [19,94].

4.7 Shrinkage and Swelling

4.7.1 Effect of Curing

Shrinkage is caused by loss of water by evaporation or by hydration of cement, and also by carbonation. The reduction of volume i.e. volumetric strain is equal to 3 times the linear contraction, and in practice, shrinkage is measured simply as a linear strain; it is thus dimensionless and is usually expressed in micro strains m x 10^{-6} [3]. Each shrinkage point in this research represents the average of eight measurements from two specimens.

The effect of various curing conditions on shrinkage and swelling of control, X, Y and Z concretes are presented in Figures 4.40 to 4.43 and Table 4.13. The Figures and data show that shrinkage behaviour of 7d wet/air-cured specimens of these mixes follows generally the air-cured specimens behaviour. The shrinkage values increased with age, the increase was sharp in the first 28 days and afterwards gradual increase was observed. However, from the slope of shrinkage curves for all mixes further increase in shrinkage could be expected.

As expected, in all mixes the 7d wet/air-cured specimens exhibited lower shrinkage values than air-cured specimens which varied from about 5 to 25%; control mix registered the highest difference of 25% compared with 6% the smallest for ZY mix, whereas shrinkage differences of mixes X and Z were the same about 20% and mix Y and ZY had 10% difference between the air-cured and 7d wet/air-cured specimens. However with increasing age the gap between the shrinkage of 7 day wet/air- and air-cured specimens was narrowed and the difference or decrease varied from 5 to 10% at the end of the curing period of 260 days. This indicates that the effect of air curing was greater on the shrinkage of different mixes compared with 7d wet/air curing for the period 7 to 28 days, with time with moisture loss through evaporation or hydration process.

In general, the 7d wet/air- and air-cured specimens of mix Y showed the highest shrinkage values followed by the control, X and Z mixes respectively. However, when comparing the 7d wet/air-cured specimens of all mixes to each other it appeared that differences are not considered to be significant, and the same can be said when air-cured specimens of all mixes compared to each other. Moreover the shrinkage developments, expressed as a percentage of 260 days shrinkage, was about the same for 7d wet/air- and air-cured specimen, 45 to 70% and 70 to 80% at 28 to 90 days, respectively.

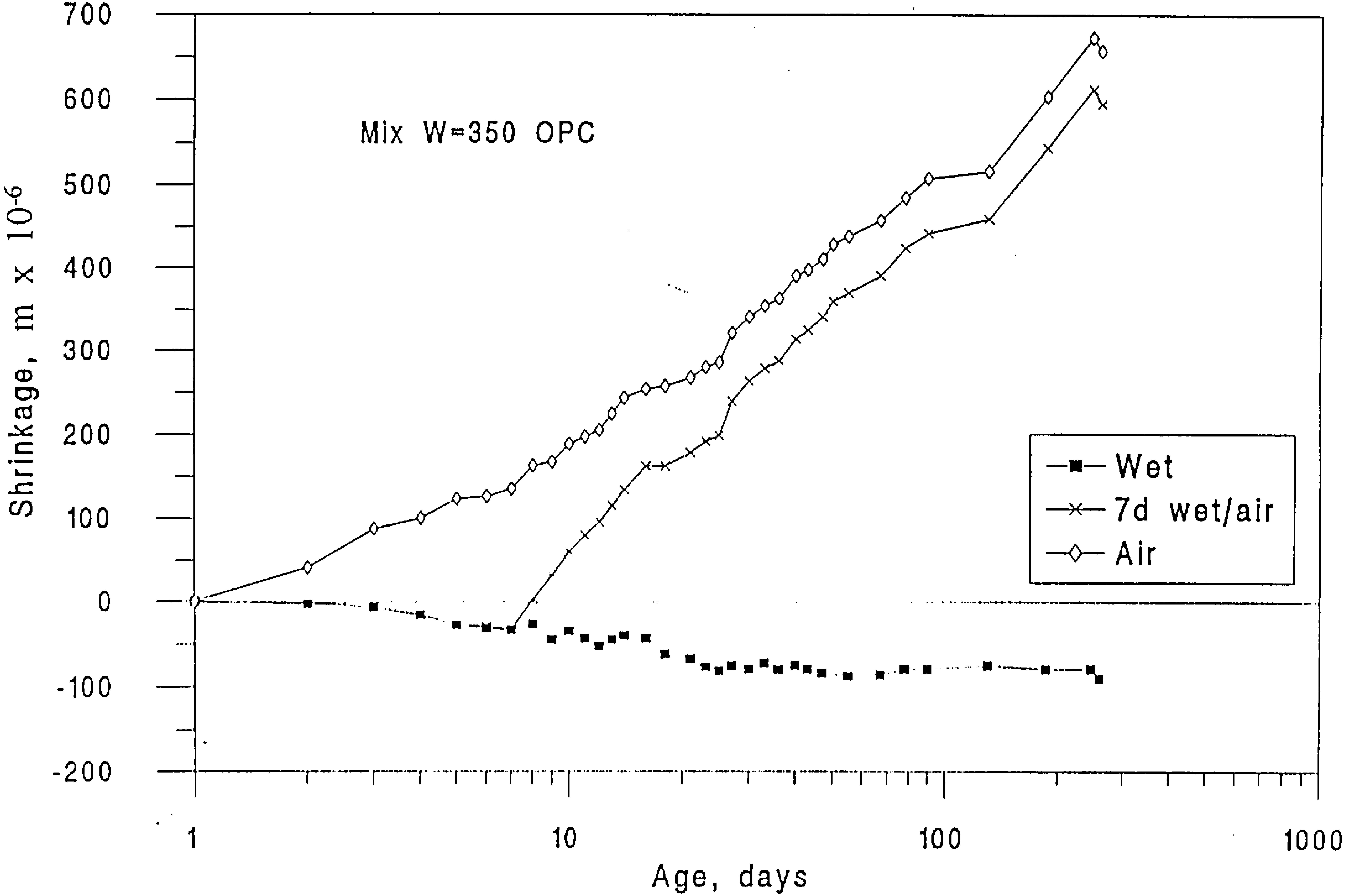


Figure 4.40 Effect of curing on shrinkage for contol mix W

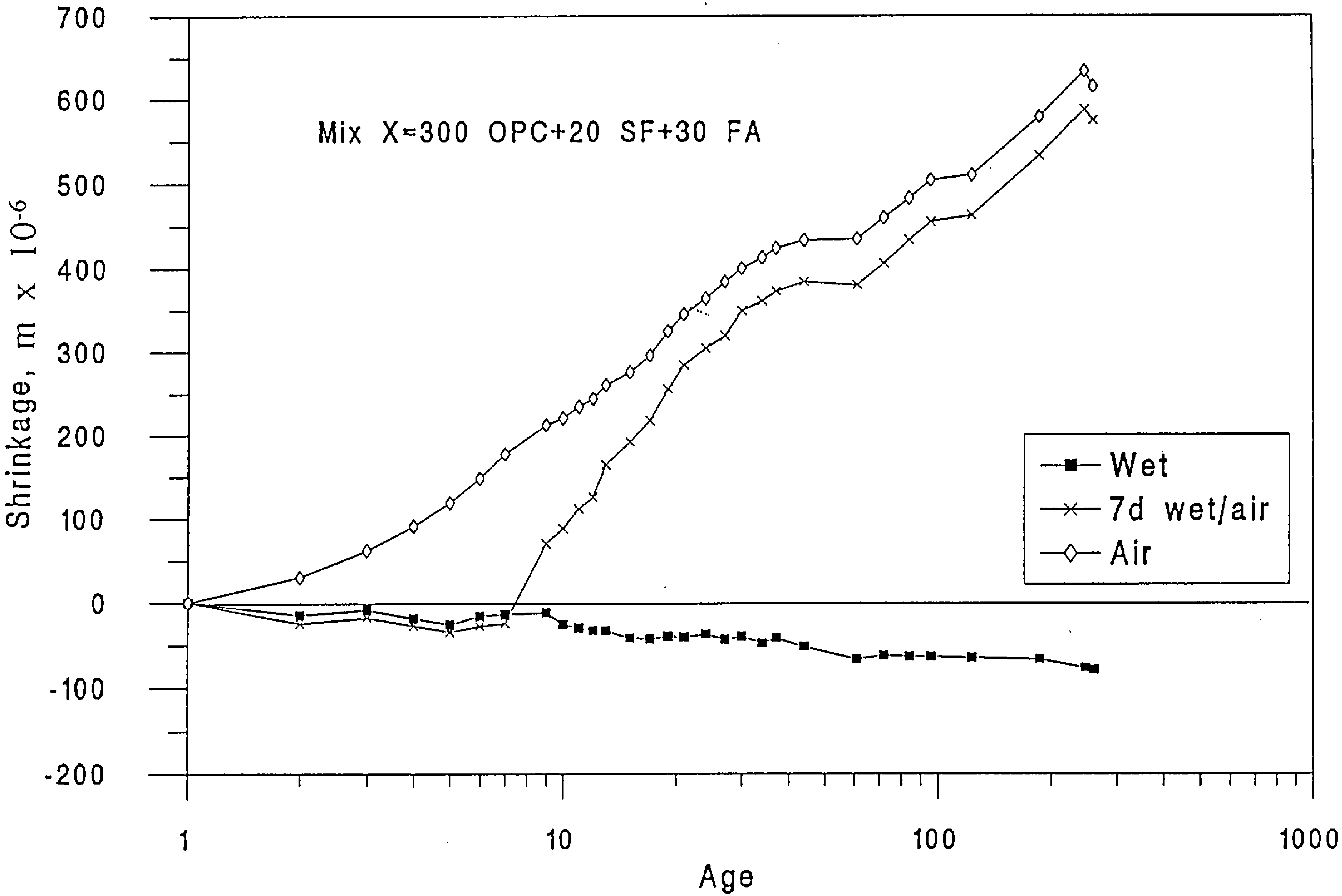


Figure 4.41 Effect of curing on shrinkage for mix X

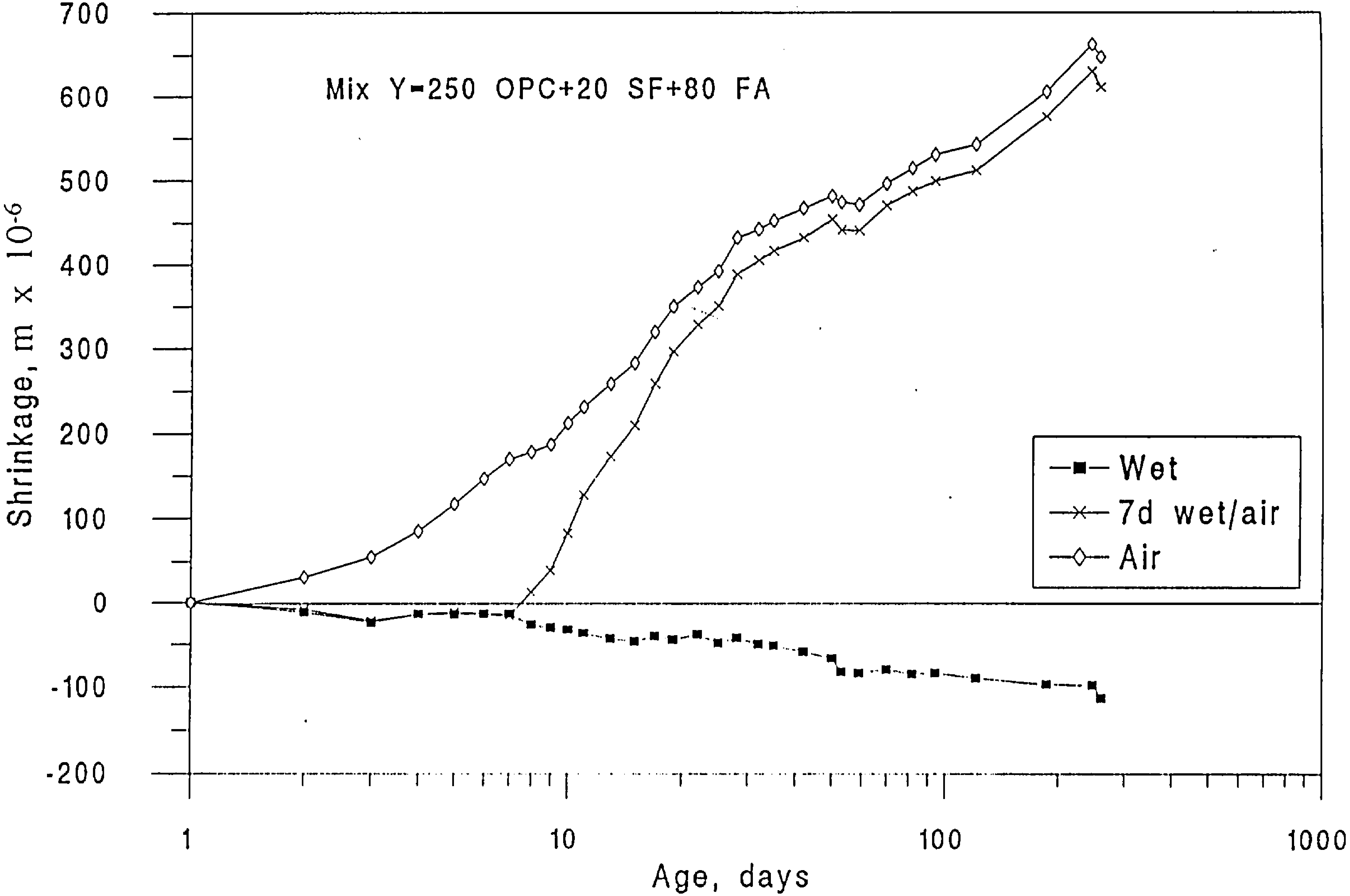


Figure 4.42 Effect of curing on shrinkage for mix Y

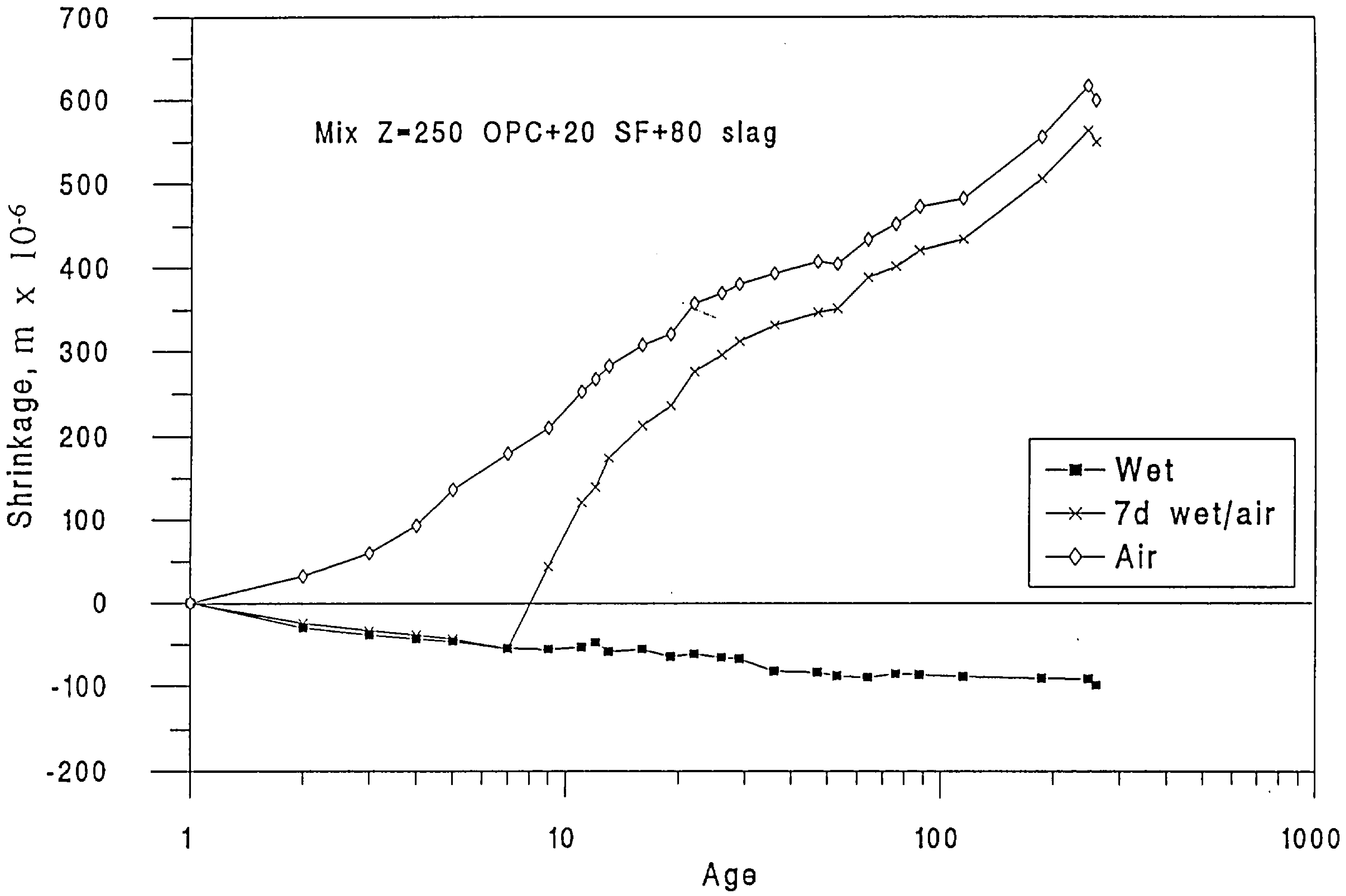


Figure 4.43 Effect of curing on shrinkage for mix Z

Table 4.13 Shrinkage and swelling of silica fume/fly ash and silica fume/slag concrete

Mix type	Type of curing	Shrinkage, microstrains				Percentage of 260 day shrinkage		
		7 days	28 days	90 days	260 days	7 days	28 days	90 days
W	7d wet / air curing	134	239	423	594	25	45	70
X		178	319	444	574			
Y		191	388	499	610	TO	TO	TO
Z		193	311	421	549			
ZX		127	301	-	-			
ZY		158	313	-	-	40	70	80
W	Air curing	135	321	484	657	20	50	70
X		177	384	494	615			
Y		170	432	530	647	TO	TO	TO
Z		179	380	473	599			
ZX		130	341	-	-			
ZY		161	332	-	-			80
W	Wet curing (Swelling)	-34	-76	-79	-90	10	30	100
X		-14	-44	-64	-83			
Y		-14	-43	-84	-113	TO	TO	TO
Z			-68	-87	-99			
ZY		-55	-86	-120	-130	40	60	110

4.7.2 Effect of Cement Replacement Material

The drying shrinkage of concrete is controlled by the volume fraction of the cement paste, and volume fraction, stiffness and maximum size of the aggregate. Also, the conditioning of the test specimen before the beginning of drying shrinkage seriously affects the test results [56]. Several investigators have reported data on the shrinkage of SF, FA and slag concretes [19,36,39,57,58], but test results are generally difficult to compare because of the different mix proportions, the different curing conditions and curing periods used before shrinkage measurements; also, most of these published data are limited to the incorporation of one cement replacement material only which is different to this study.

Figures 4.44 to 4.47 show the shrinkage and swelling behaviour of control X, Y, Z, ZX and ZY concretes. The shrinkage results show that when subjected to continuous drying i.e. air curing, concretes incorporating FA/SF and slag/SF have initially higher shrinkage than that of the control mix up to 28 days, probably due to the action of mineral admixtures, particularly SF. The shrinkage strain for 80 kg/m^3 FA mix was slightly higher than for those incorporating 30 kg/m^3 FA, 80 kg/m^3 slag and control mixes at all ages (Fig 4.45 and 4.46). This shows that at the same two replacement levels, the inclusion of 80 kg/m^3 FA in a mix designed for the same workability might increase the paste volume than the corresponding 80 kg/m^3 slag mix, and with higher than 25% FA replacement drying shrinkage may be expected to increase on the assumption that the drying shrinkage of concrete is a function of the volume percentage of paste present in concrete. However, the figure shows that the difference between drying shrinkage values of control X and Z was found little, although a close examination of results show that 80kg/m^3 slag concrete performed better (10% lower than the control), confirming its superiority over the other mixes as the strength, dynamic modulus and pulse velocity data show. In fact the use of slag to replace cement had little influence on drying shrinkage of concrete and thus the long term shrinkage of well proportioned and adequately cured slag/SF concretes is likely to be lower than that with the same FA replacement. Distinct benefits can be obtained through the continued strength development of slag/SF concrete and this will be reflected both in shrinkage and dynamic modulus. The magnitudes of shrinkage shown in Figures 4.45 and 4.46 were of the order as that reported by Swamy and Buikni [19] for 50 and 65% slag concretes subjected to continuous dry and initial 7 day water curing before drying. The work of Neville and Brook [11] showed that for concretes subjected to a drying environment of 60% relative humidity at 20°C after period of 28 day storage in water, the drying shrinkage of the 50% slag mix was about 10% lower than that of the OPC control.

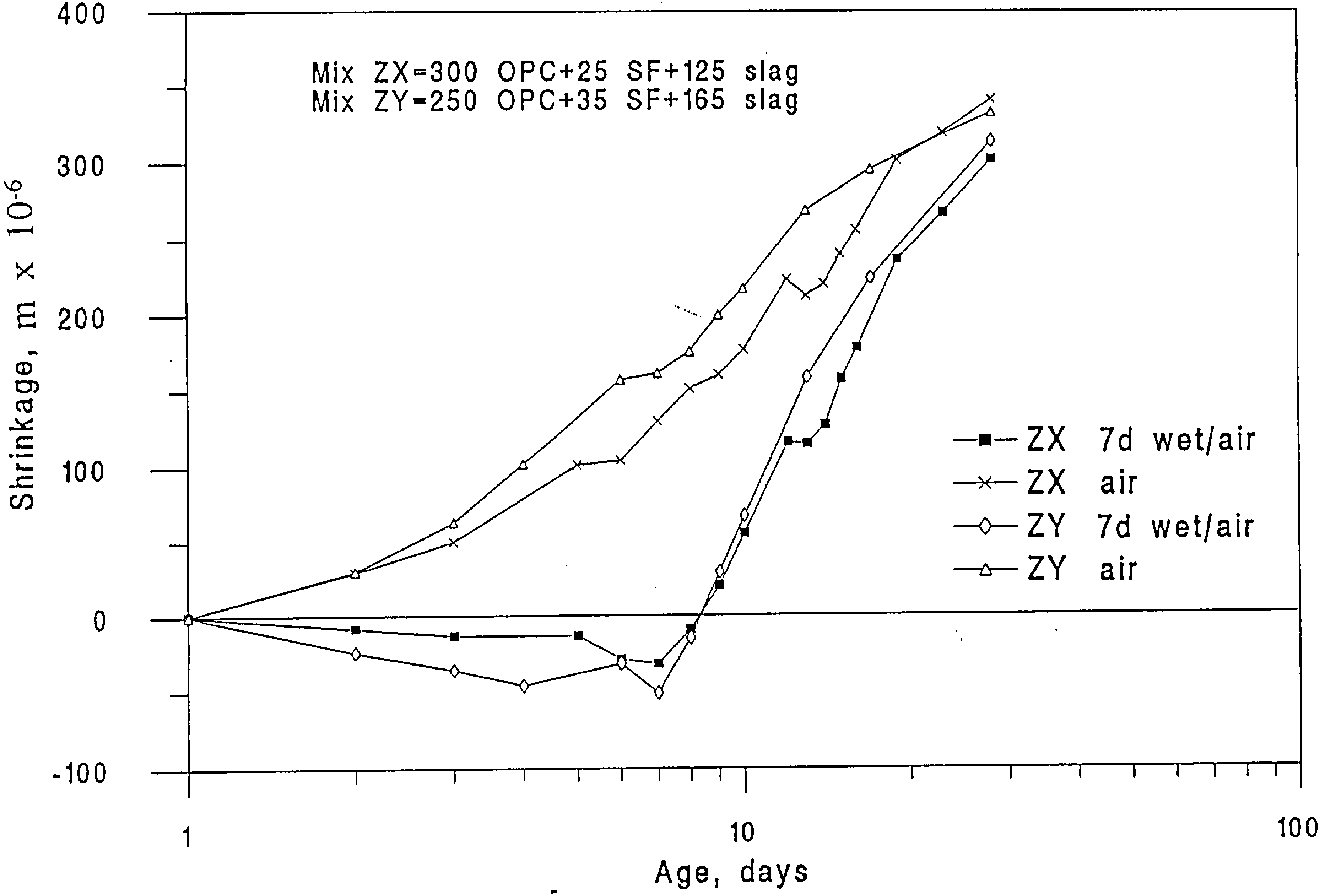


Figure 4.44 Effect of curing on Shrinkage for mixes ZX and ZY

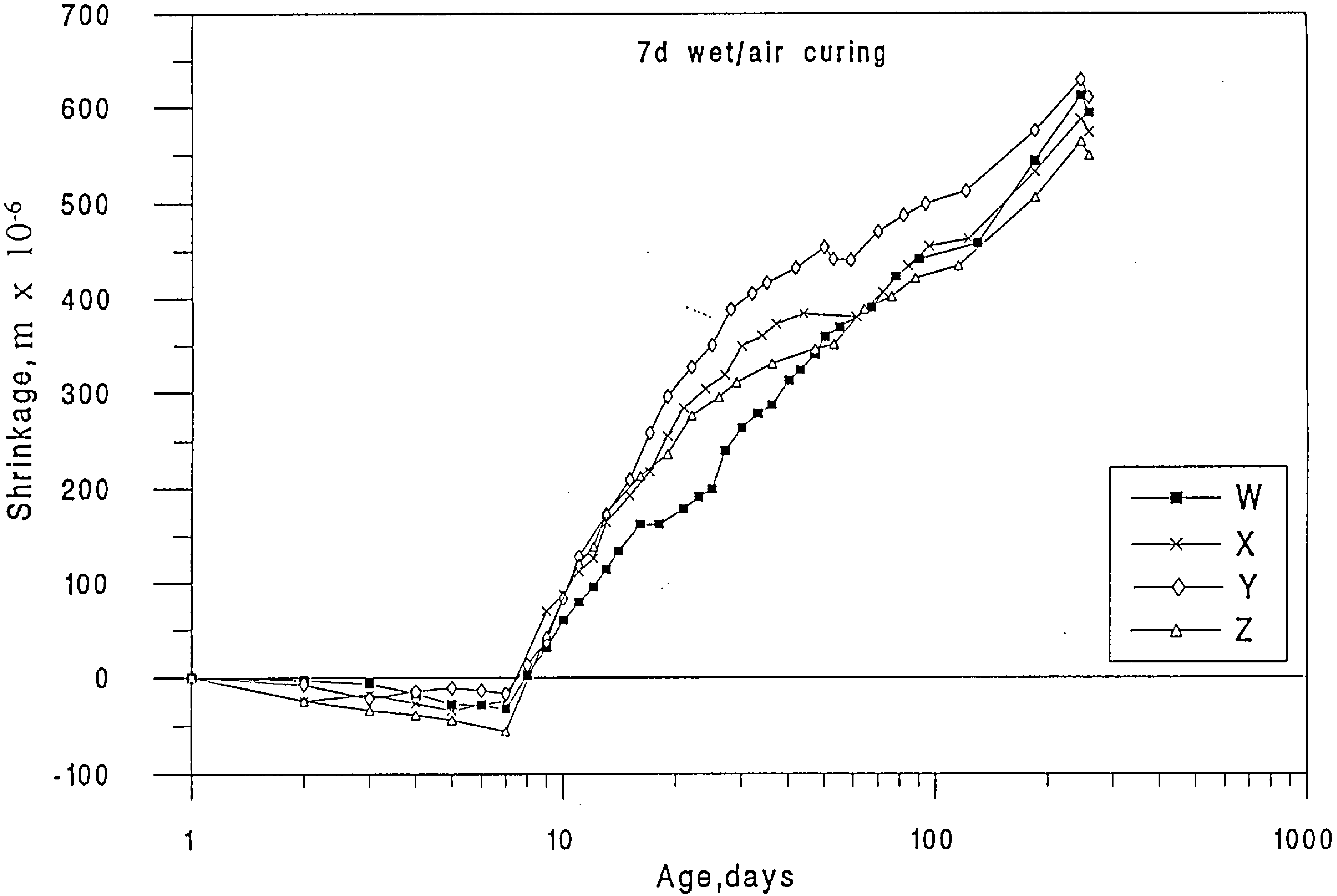


Figure 4.45 Effect of mineral admixtures on shrinkage for mixes W,X,Y and Z

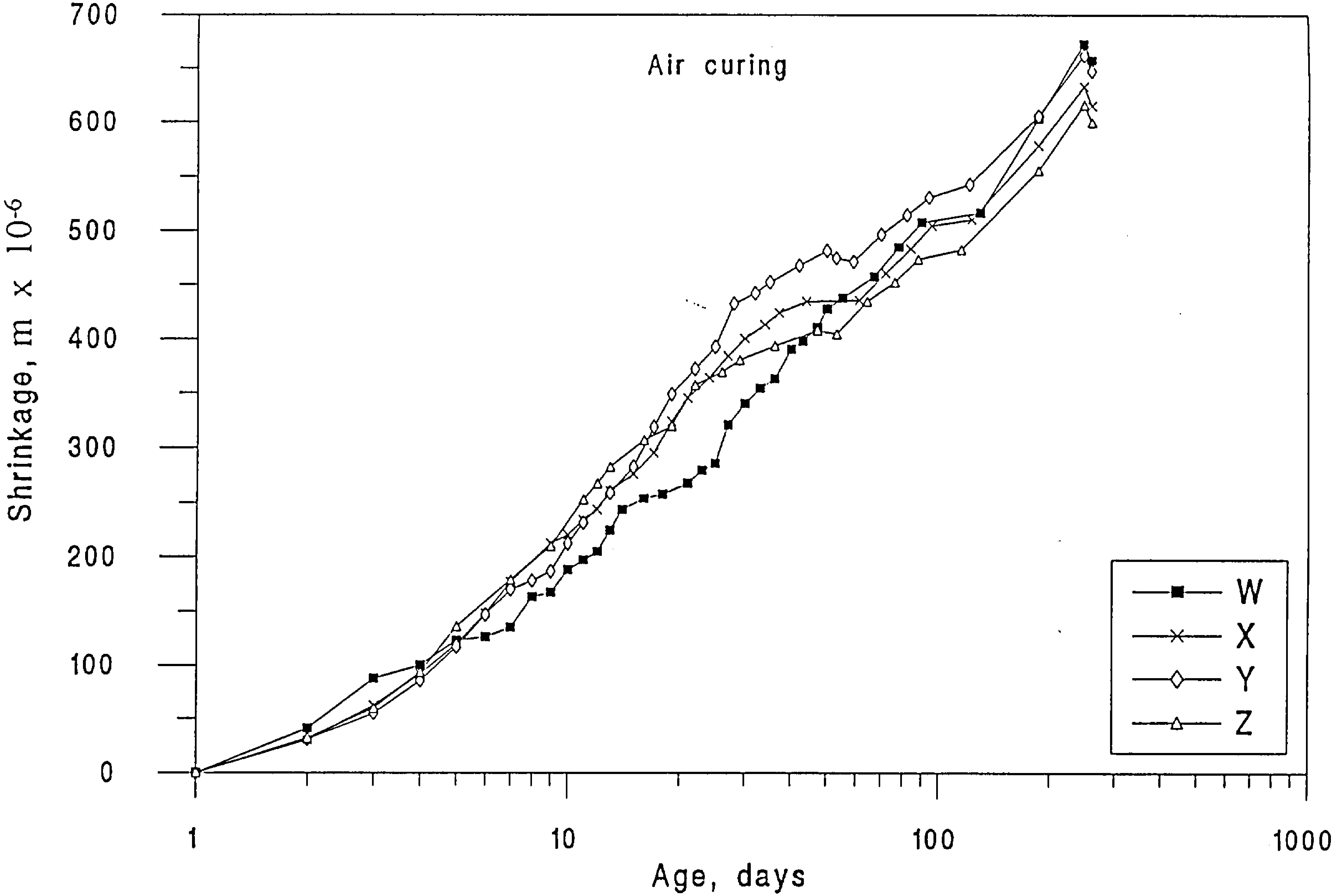


Figure 4.46 Effect of mineral admixtures on shrinkage for mixes W,X,Y and Z

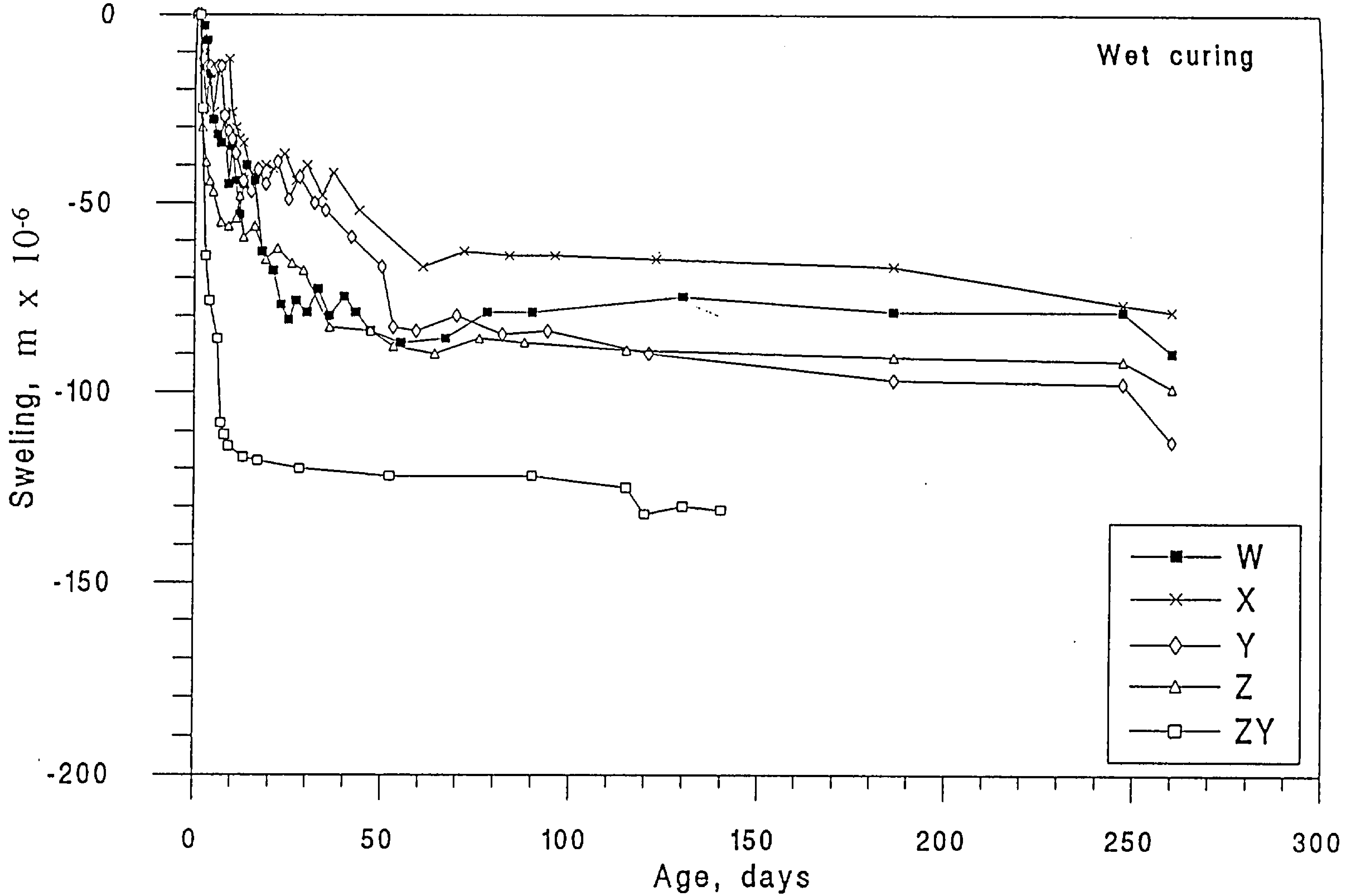


Figure 4.47 Effect of mineral admixtures on sweling for mixes W,X,Y,Z and ZY

In regard to SF, the data from drying shrinkage tests by different researchers show that the long-term shrinkage of concrete is not affected significantly by the addition of SF, especially when the water content of the concrete mixture has not been changed, which was the case in mixes for the study.

The contribution of SF to drying shrinkage was cited by Khayat and Aitcin [83]. The concretes had had 0, 10, and 20% cement replacement with SF and W/ (C+SF) ratios between 0.37 and 2.11. All concrete samples were moist cured for 7 days before drying in air at 60% RH. For concretes with W (C+SF) ratios less than 0.6, the SF mixtures were found to exhibit lower shrinkage values than non SF concretes. Johansen [8] measured drying shrinkage of concrete prisms that were exposed to a drying environment (50% RH) immediately after demoulding and after 28 days moist curing. The concretes had SF addition as 0, 5, 10 and 25% and W/(C+SF) ratio of 0.37 and 1.06. It was concluded that for concrete with W/(C+SF) <0.6, no significant differences in drying shrinkage existed between the reference concrete and SF concrete containing up to 10% SF. Concrete containing 25% SF had greater shrinkage values than non-SF concretes.

Also there are many published data on the drying shrinkage of SF concrete and the results lead to similar conclusions. Hence, the general conclusion is that the shrinkage of the different mixes used in this study were most probably not affected by the addition of SF, and if there would be any increase in drying shrinkage it would be of little practical significance.

Similar behaviour of drying shrinkage is also shown by control X, Y, Z, ZX and ZY concretes when exposed to initial 7 day water curing before drying (Figure 4.45). The average shrinkage of 80 kg/m^3 FA mix at 260 days was approximately 610 x 10^{-6} slightly higher than control mix, 590x10^{-6}; the corresponding average shrinkage of 80 kg/m^3 slag mix was 550 x 10^{-6}, and 10% lower than both control and Y mixes and 5% lower than X mix. This difference shows that increasing the replacement level of FA from 30 to 80 kg/m^3 increased the shrinkage of the specimens and further increase in FA addition on an equal mass basis would increase the paste volume and hence the drying shrinkage will be increased if the water content remained constant; whereas mix Z results indicates that addition of slag resulted in slightly less drying shrinkage compared with portland cement concrete. All the benefits of slag replacements, even at high additions, can be realised if the blended cement is allowed to fully hydrate and achieve its strength and durability potential [19].

The swelling strains when exposed to a continuous wet condition of control, X, Y and Z mixes are shown in Figure 4.47. The Figure shows that all swelling strains were obtained during the period of 7 to 60 days (and 100% of it was at 60 days age), after which all readings showed a slight reduction, and then they remained relatively unchanged with age as the curing continued. This much expansion within this period for concretes was indicative of the ability (and need) to absorb large amounts of water needed to continue the hydration process, and of course, of the need for the continued presence of moisture to enable its pozzolanic action to continue. Also it indicates the need for longer wet curing for concretes with high FA and slag replacement levels. If this water requirement is not satisfied, both pozzolanic and cementitous activity are arrested, leading to strength loss, void formation, and long-term lack of durability [19]. Thus, the losses in flexure strength and pulse velocity values in 7d wet/air- and air-cured specimens might be probably as a result of the stoppage of cementitous activities of mineral admixtures. At 28 days, the expansion of control concrete was 70% higher than both X and Y concretes and 10% higher than Z concrete; and the swelling of control mix at this age was 25% of the corresponding drying shrinkage which is about double than the swelling of X and Y mixes at their corresponding drying shrinkage. This shows that even FA/SF mixes were in need of water but this demand did not appear up to about 28 days after which both mixes showed a similar demand to that of the control and Z mixes. Hence a longer period of wet curing for FA/SF concretes could be suggested to fulfil their pozzolanic potential, and that even 7 days of wet curing are inadequate for high levels of FA and slag replacements if the full strength potential of these mineral admixtures is to be realised and durability assured.

At 260 days, however, the swelling of Y and Z mixes was about 25% of their corresponding drying shrinkages compared with about 20% for both control and X mixes. This is understandable, mixes Y and Z were the same because they contain the same replacement level of SF and FA or slag (about 30%) whereas mix X contains 10% replacement,the effect of which such on swelling seems to be comparable to that of control mix although it showed the least swelling values (Figure 4.47). On the other hand, comparing mixes Y, Z and ZY of the cement content (250kg/m3), the concrete with high slag replacement level (165kg/m3) showed about double the swelling strains of Y and Z mineral admixture concretes, indicating strains of Y and Z mineral admixtured concretes, indicating the need for much longer wet curing for concrete with high slag replacement levels; and the same can be said for high FA replacement levels concrete.

4.8 Conclusions

1. To obtain the required workability and high-early-age strength development the use of superplasticizer was necessary.

2. The water demand in all FA/SF and slag/SF concrete mixes was slightly higher than control mix because of very fine particles and high surface area of SF. This was lowered by the addition of a superplastisizer. However, with high slag replacement levels workability was enhanced and 50% less superplastisizer was required.

3. The low early-age strength of OPC concrete incorporating either FA or slag can be increased by the use of SF. The gain in strength is, in general, directly proportional to the percentage of the SF used.

4. At 7 days and beyond, with minor exceptions, the loss in compressive strength due to incorporation of FA and slag can be compensated for by a given addition of SF, regardless of curing conditions. This is also true for flexural strength.

5. The results show that all mixes conditioned in the three curing regimes were able to develop the required 28 d compressive strength of 50 MPa, in fact they reached strengths in excess of 50MPa, about 60MPa, except for concrete specimens of mix ZY cured in air where it reached about 90% of its target strength and continued to hydrate and showed modest improvement up to 4 months. Thus slag replacement can bring real benefits when no water curing occurs and forms are removed within one day.

6. The 7d wet/air-cured specimens exhibited slightly higher compressive strength values in all concrete mixes, about 5% higher than the wet ones.

7. The early-age-strength of FA and slag concretes decreases as the replacement level increases.

8. Air-cured specimens displayed the lowest compressive and flexural strength values in all concrete mixes considered and at all ages of curing compared with wet- and 7dwet/air-cured specimens. This is due to no curing, where there wasn't ample quantity of water in the specimens for hydration, hence lower values of compressive and flexural strength were obtained.

9. Under 7d wet/air- and air-curing conditions, all specimens indicated flexural strength loss after about 90 days, presumably due to non-uniform moisture distribution, and the influence of air curing was greater on this property compared to wet- and 7dwet/air- cured condition. Compressive strength did not show any retrogression.

10. The 30 and 80 kg/m^3 FA/SF and 80 kg/m^3 slag/SF concrete mixtures achieved nearly the same compressive strength as control concrete at 7 days. Some retardation of strength was still observed for slag concrete mixture with 125 and 165 kg/m^3 cement replacement level until age of 7 days.

11. One-day compressive strength was still relatively low, about 60% of the corresponding control concrete strength at 80 and 125 kg/m^3 slag replacement level, and about 35% at 165 kg/m^3 slag replacement level concretes were about 90 and 65.

12. The highest values of dynamic modulus for all concrete mixtures were obtained under continued wet conditions of curing followed by specimens cured under 7d wet/air and air curing conditions, respectively.

13. When compared with wet curing dynamic modulus under air drying without water curing produced significant reductions in the modulus of FA/SF and slag/SF concretes, about 20% at age of 260 days. Whilst with 7d wet/air curing the loss in modulus was about 15% at same age. Modulus of control concrete was less affected by such drying conditions, the reduction was nearly 5% between both wet and 7dwet/air, and air curing. In other words the dynamic modulus of FA/SF and slag/SF concretes are more sensitive to drying by air and 7dwet/air- curing than OPC concrete.

14. At the age of 28 days, the 7dwet/air- and air-cured specimens exhibited their largest modulus values and does not show any further improvement in modulus development beyond this age, whilst the wet cured ones continued showing increases in dynamic modulus due to the direct consequence to continued hydration process which produced intergrown microstructure.

15. Dynamic modulus is more sensitive to the incorporation of FA than slag, and with relatively higher replacement levels of FA greater reduction in modulus would result.

16. Under wet curing conditions, there is little difference in dynamic modulus between FA/SF, slag/SF and OPC control concretes. However a close examination of data revealed that 165kg/m^3 slag obtained the highest modulus.

17. Although 7dwet/air-cured concretes had slightly higher compressive strength at 28 days than concretes subjected to continous wet curing the former showed a loss in dynamic modulus of about 15% compared to the latter, obviously due to internal microcracking and insufficient hydration. In fact all concretes showed a strength increase of 20 to 25% from 28 to 260 days, and yet does not registered any development in their modulus from that of 28 days when exposed to drying in air and 7dwet/air curing.

18. Prolonged drying has adverse effects on dynamic modulus and can create internal microcracking not readily recognized by compressive strength values. Except for the case of continued water curing, compressive strength should not be used as a criteria of concrete quality after 28 days, since flexural strength, dynamic modulus and pulse velocity vary quite differently from compressive strength when insufficiently cured FA/SF and slag/SF concretes begin to dry with time.

19. The wet-cured specimens of all mixes yielded the highest pulse velocity values followed by 7d wet/air-cured specimens and then the air-cured ones.

20. At 260 days all wet-cured mixes were 5 and 7% higher than 7d wet/air- and air-cured ones.

21. The effect of curing regimes on pulse velocity is similar to that on dynamic modulus of elasticity.

22. For each mix the 1 and 28 days values of pulse velocity were similar for the three curing conditions, i.e. the effect of curing regimes being more pronounced at 28 days and beyond.

23. Control and FA/SF and slag/SF concretes performed similarly in the wet curing condition, whilst under the worst conditions of curing the 80 kg/m^3 FA/SF concrete recorded lower pulse velocities at all ages.

24. Pulse velocity measurements indicated the beginning at internal microcracking in FA/SF and slag/SF concretes with air and 7d wet/air curing. Drying can thus have adverse consequences on the long term durability of such concretes; however, this effect on the intense microstructure of concrete could not be indicated by compressive strength measurements.

25. In all mixes the 7d wet/air-cured specimens exhibited lower shrinkage values than air cured specimens which varied from about 5 to 35% at 28 days and 5 to 10% at 260 days, indicating the greater effect of air curing on shrinkage of different mixes compared with 7d wet/air curing, and with time with moisture loss through evaporation or hydration the 7d wet/air curing had little influence on the magnitude of shrinkage and longer period of curing is required.

26. The shrinkage of FA/SF concretes are slightly higher than those of slag/SF and control concretes.

27. When exposed to wet curing, the concrete with 165kg/m^3 slag replacement showed about double the swelling strains of control and other mineral admixtured concretes during the period 7 to 28 days, indicating the need for much longer wet curing for concrete with high slag replacement levels.

28. The results of this chapter indicate that continued exposure to a drying environment of inadequately cured FA/SF and slag/SF concretes can adversely affect their long-term-durability. They also show that even 7 days of wet curing are inadequate for high level of slag replacement if the full strength and durability potential of the slag are to be realized. The results also confirmed that slag/SF concretes performed better than FA/SF concretes, however, both concrete mixtures can be designed to give consistent 28-day high strength results.

CHAPTER FIVE

TEST RESULTS AND DISCUSSIONS OF PART II MICROSTRUCTURAL PROPERTIES

5.1 Introduction

It is generally accepted that many of the basic physical and mechanical properties of materials depend on their pore structure, (i.e. the shape and size of the pores) and on the distribution of the volume of the pores. Pore size not only influences the chemical reactivity, but it can also influence engineering properties such as strength, modulus of elasticity, volume stability, and environmental resistance [68,95]. A construction material such as concrete made containing mineral admixtures (FA, SF and slag) is a typical example of materials affected by pore structure and pore size distribution. Hardened cement paste that serves as the binder in concrete is regarded as a porous material and therefore its porosity and pore structure have to be investigated.

In this investigation, the mercury intrusion prosimetry (MIP) technique was employed to determine the porosity and the pore size distribution of various concretes containing mineral admixture subjected to three different curing conditions.

5.2 Details of mixes and sampling

Blends of FA, SF and slag with OPC generally possess properties equivalent to, or in some ways superior to, typical OPC concretes and if proper water-curing is applied porosity is reduced and pore size distribution may be refined leading to improvements in the durability of concrete.

The objective of the experimental work was to determine the pore structure of OPC and blended cement concretes by measuring the porosity and pore size distribution. Three curing conditions were employed for studying the pore structure of the different concrete mixes. Concretes of cements blended with materials such as FA, SF and slag, are reported to be very sensitive to unfavourable curing [96,97], owing to their low rate of hydration compared with ordinary Portland cement (OPC). Absence of water when FA, SF, and slag particles start hydration, therefore, results in low quality concrete, which can lead to higher rates of ingress of harmful substances such as chlorides [98]. Six different concrete mixes were studied, mixes W, X, Y, Z, ZX and ZY, details of

Table 5.1 Details of mixes W to ZY and parameters examined

Mix proportions, kg/m^3								
Mix	**Cement OPC**	**FA**	**SF**	**Slag**	**Water**	**Fine aggregate**	**Coarse aggregate**	**Superplasticizer***
W	350	-	-	-	157.5	600	1225	1.20
X	300	30	20	-	157.5	600	1225	1.35
Y	250	80	20	-	157.5	600	1225	1.36
Z	250	-	20	80	157.5	600	1225	1.48
ZX	300	-	25	125	202.5	600	1225	0.60
ZY	250	-	35	165	202.5	600	1225	0.68

Parameters examined

1- Cement and mineral admixtures content

2- Curing regimes

I- continuous wet curing

II- 7 days wet curing followed by air curing

III- air curing

3- Porosity

4- Pore size distribution

5- Threshold diameter

6- Compressive strength vs. porosity

7- Compressive strength vs. large pore volume>1000A

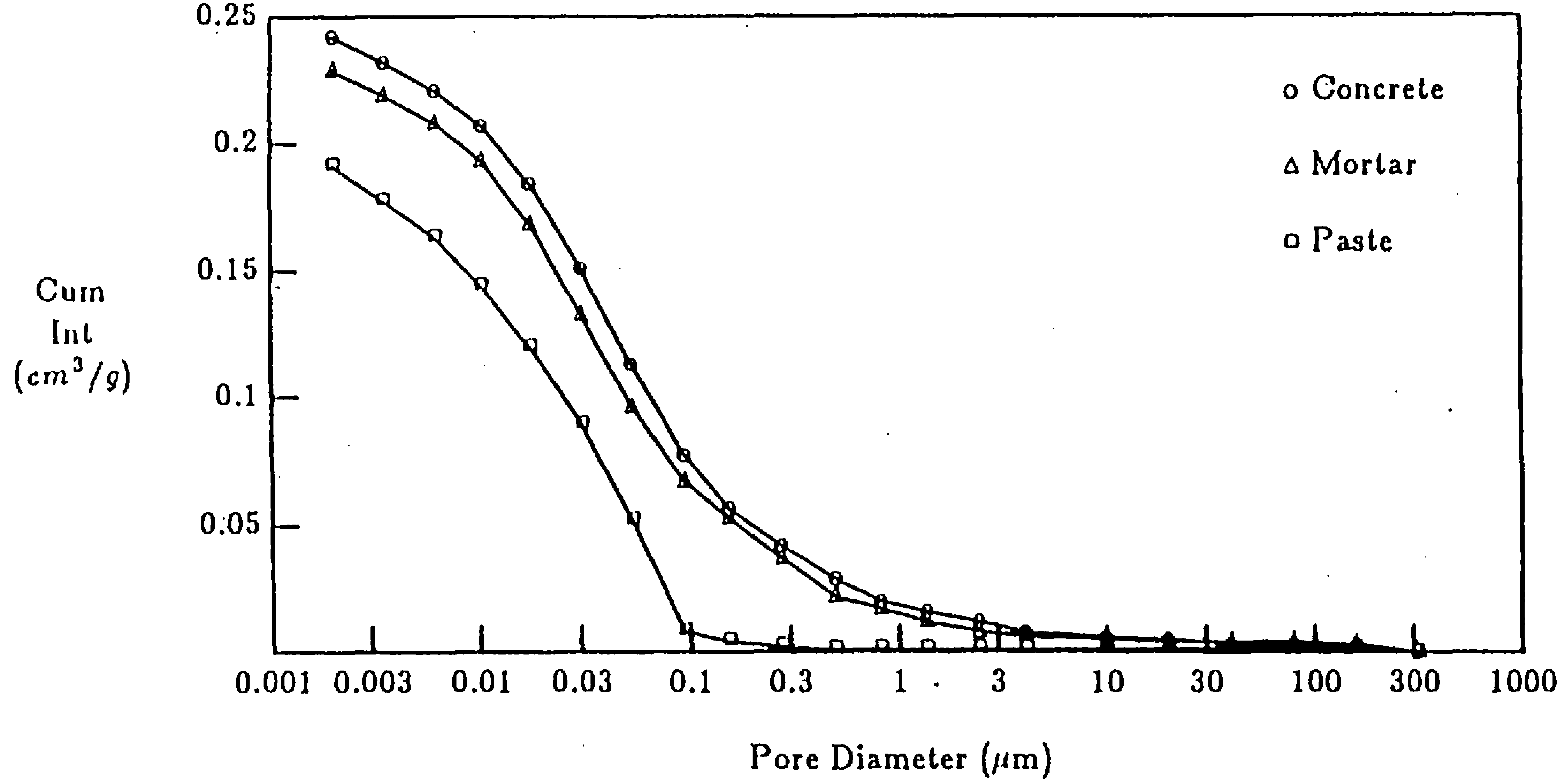
* weight % of cementitious content

which are given in Table 5.1. The water/cementitious materials ratio for all the mixes was kept constant at 0.45. A superplasticer (SP6) was added to all concrete mixes to maintain a constant workability of 100 to 150 mm slump. Further details of the materials used in these mixes are given in Chapter 3.

Sample preparation is one of the important factors which affects the results of MIP measurements. In most of the investigations, to make the study easy, the pore structure as well as permeability measurements are conducted on cement paste or mortar samples cored from cubes or larger samples, and it is usually considered that hardened cement paste or mortar prepared in this way is sufficiently similar in properties to that actually produced within the concrete under field conditions. This practice is thought not to represent the realistic bulk concrete encountered in practice. However, some research has indicated that the paste which forms near the interface with an aggregate particle has a different microstructure. Winslow and Liu [99] carried out research to see that when paste forms in the presence of aggregate, is it has the same pore structure as it has in the absence of aggregate. It is this pore structure which greatly influences such crucial concrete properties as strength, shrinkage, permeability, and durability [99]. The essential findings of their study is that the presence of aggregate does, indeed, influence the microstructure of the paste that forms around it, and that cement paste forms in concrete has a pore structure that is different from that in plain paste. They [99] concluded also that the paste in concrete is more porous, and that the majority of the extra porosity has a larger diameter than found in plain paste; and these are the pores which are most likely to affect properties such as permeability and durability in an adverse way. An important example of their findings is demonstrated in Figure 5.1.

Also the position from where the specimen is obtained for analysis influences mainly the measured properties of concrete or cement paste. The pore volume varies substantially within the body of a cement or concrete matrix. It is reported [100] that the top face of a specimen will possess the highest porosity followed by those on the side positions, whereas the middle (core) and bottom position will exhibit the lowest total pore volume, and so is the percentage of volume of large pores.

Hence, for pore structure measurements carried out in this study using mercury intrusion porosimetry (MIP), samples were taken from the middle (core) of 100 x 100 x 500 mm concrete prisms cast for this purpose as shown in Figure 5.2. The mortar from the middle position of the concrete specimen was carefully obtained without any coarse aggregate particles being present, since the presence of such particles distorts the pore



Figrure 5.1 Difference in the pore size distribiutions of the paste,mortar and concrete for more hydrated samples, w/c=0.45 [99]

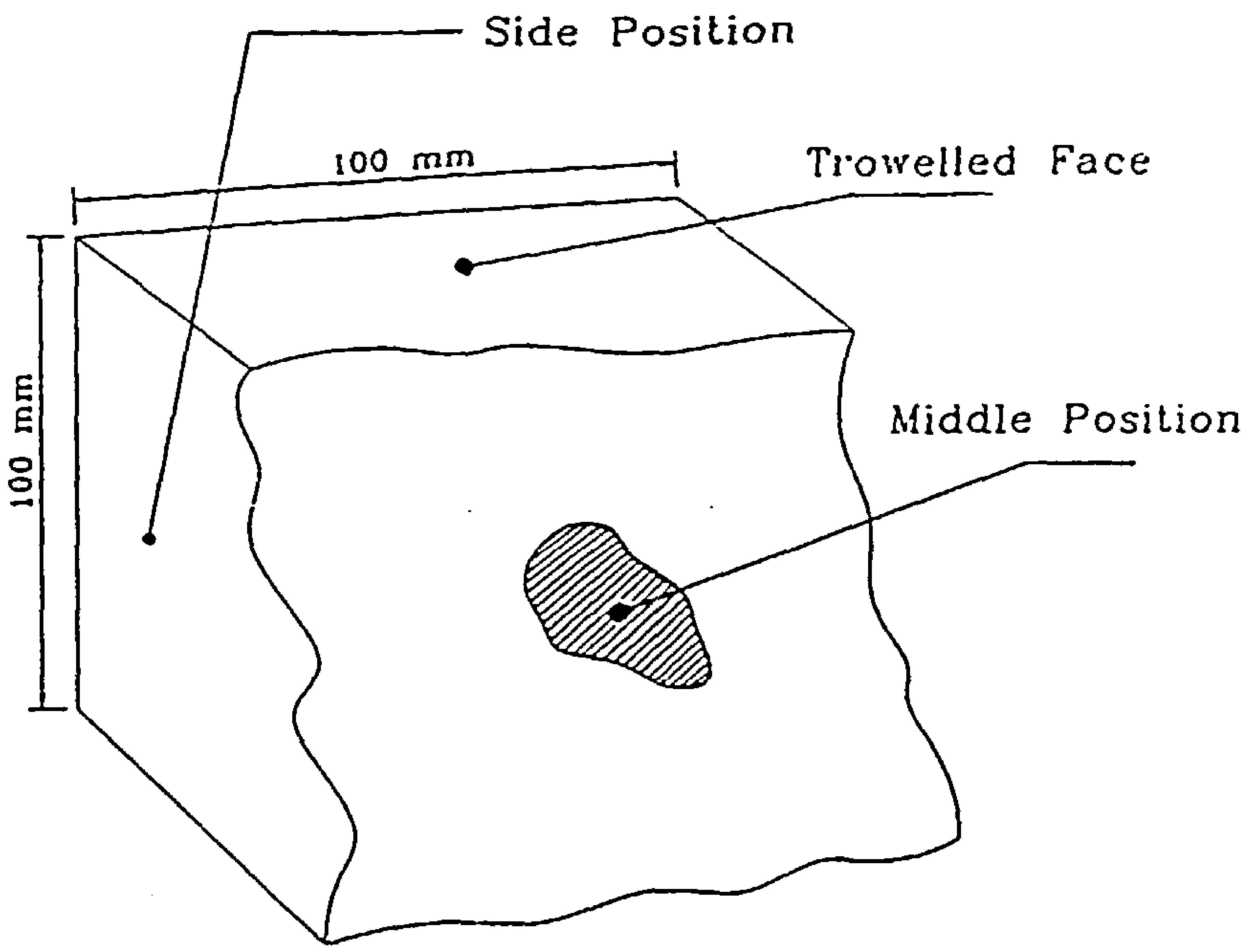


Figure 5.2 Location of sample for MIP test(section through vertically cast prism)

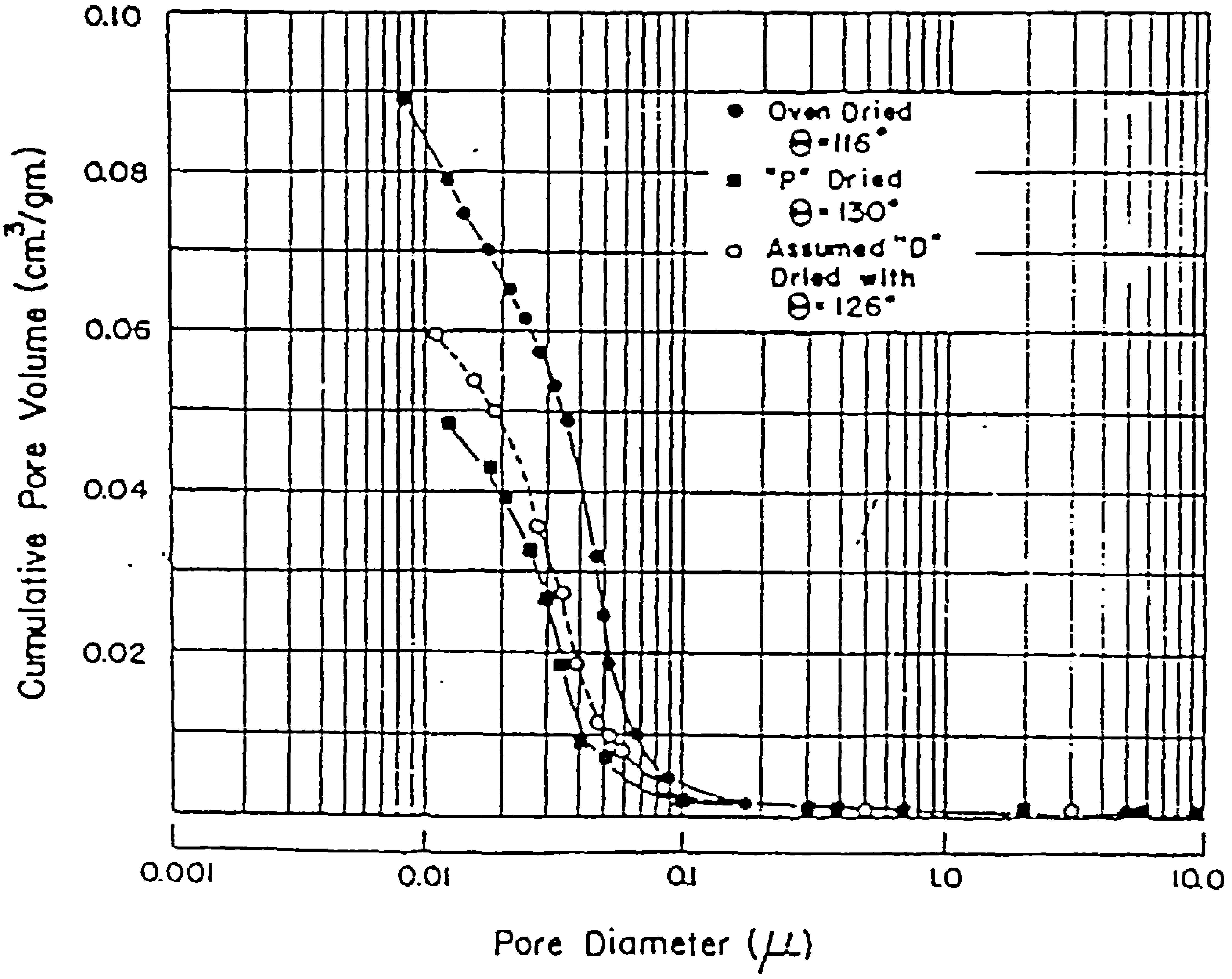


Figure 5.3 Influence of drying procedure on measured pore size distribution Cement has w/c ratio of 0.4;hydrated 158 days .[101]

size distribution and affects, to a large extent, the interpretation of the MIP results. The weight of each sample ranged between 1.5 to 2.5 gm, which was adequate for MIP testing. All samples for pore size distribution were made up of very small broken pieces, oven dried, and then tested in the bulk condition, that is, not ground to a powder. In most investigations [23,101] it is customary to use fragments of a cube of a cement paste, mortar or concrete, after breaking it. Sometimes porosimetry is conducted on cores of cement paste or mortar obtained from larger samples [102]. Grinding the sample to powder could create micro-cracks which may distort the pore size distribution.

5.3 Pore size distribution determination

5.3.1 Theory

Mercury porosimetry technique is based on the fact that a non-wetting liquid (one forming a contact angle with a given solid greater than 90 degrees) will intrude open pores of the solid only under applied pressure [101]. The pressure required to force the mercury is a function of the contact angle, the surface energy of the liquid, and the geometry of the pores; the pressure increases as the pore diameter decreases. For the case of cylindrical pores the relation given by Washburn [103] is

$$p = \frac{-4\gamma Cos\theta}{d}$$

where:

p = pressure required to intrude a pore
d = diameter of the intruded pore
γ = surface energy of the liquid, and
θ = contact angle between the liquid and the pore wall.

Mercury is almost always used as the liquid; its practical advantages include low vapour pressure, relative inertness in terms of chemical reactivity, and the fact that it is normally non-wetting for most kinds of surfaces [101].

There are some factors and assumptions contributing to errors in the mercury porosimetry technique. Some of these factors are discussed in the following section.

Pore Geometry

The Washburn equation, which is used to calculate the pore size, is based on the assumption that the pore structure consists of straight right angle cylindrical pores. This assumption is not always valid as reported by Ritter and Drake [104] and other researchers [105]. They reported that the extrusion curve does not coincide with the intrusion curve and was attributed to the presence of the ink-bottle pores, which trapped in mercury. However, the uncoincidence is accepted and well known, it was also found in the work presented in this thesis.

Another error factor [101], because of operational characteristics of the intrusion measurement, is the term "pore diameter" which does not necessarily represent the actual pore diameter, but refers to what might be called "pore entry diameter". This means that the pore has an entry diameter smaller than that of the pore itself, and that the internal pore will be intruded only after sufficient pressure is applied to intrude the narrower pathway. Thus, volume of narrow entryways pore are not measured and a shift of pore size distribution curve to the finer pores could result which does not represent the actual curve.

On the other hand, isolated pores having no communication with the exterior of the sample cannot be measured in any event, regardless of the pressure used [101]. The measured pore size distribution curves are thus lower bound curves; the true curve would show a greater cumulative volume of pore space to the extent of that isolated pores.

Compressibility

The compressibility of mercury is another source of error that requires a small correction. The mercury is being compressed as the pressure is increased, but the required correction is much less than the absolute loss in the volume of the liquid since the pentrometer containing the mercury is also being compressed at the same time [101,106]. Correction is made by measuring the effect of pressuring in the same pentrometer filled with mercury only, that is, without any sample being present. In the present work this correction was carried out.

The temperature increase of mercury as it is being compressed tends to mask some of the compression, and it is necessary to allow the mercury to return to its original temperature [101,107]. However, in the design of the porosimeter used in this research

[106] the corrections due to compressibility and temperature are taken into account so as to yield negligible residual error.

Sample evacuation

Before the initial mercury filling step is carried out in mercury porosimetry measurement, the dry sample is put into a pentrometer and is subjected to vacuum pressure for getting rid of any air entrapped inside the sample. This is to allow the mercury to penetrate into small pores. Failure to do evacuation for the residual air remaining in the sample and pentrometer results in an error in the intrusion volume measurements [101,105]. However, the MIP machine used in this study automatically evacuates the sample, fills them with mercury and pressurizes them.

Contact Angle

For the measurement of actual sizes of the pores in a porous sample, the correct value of the term ($-4\ \gamma\ \text{Cos}\theta$) should be shown. The value of surface tension of mercury (γ) is usually taken by researchers to be 484 or 485 dyne/cm, whilst the variation is in the contact angle.

The contact angles of mercury with the pore walls of a large variety of materials often quoted are in the range of 112-142°, and the most commonly used are 130° or 140° [106,108]. In most of the published work on porosimetry, the contact angle used is assumed not determined. Measurement of the contact angle can be performed by drilling holes of known diameters in a sample, and inserting wires into the sample while it is still plastic, and measuring the pressure required to intrude mercury into these holes. Winslow and Diamond [101] drilled holes into cement paste specimens and found out that the measured contact angle is affected by the method used to dry the specimens. Their study indicates a contact angle of 117° and mercury surface tension of 484 dyne/cm for oven dried specimens. Shi and Winslow [109] also measured the contact angle for oven dried specimens at different ages and it was found to be in the range of 123 to 135°. However, comparison of the same type of material, prepared and cured in the same way, assuming one fixed value for the contact angle may not change the ranking of the mercury porosimetry results to a significant degree. In this work a fixed value of 130° contact angle, between the mercury and the surface of concrete (mortar), and surface energy of sample 485 dyne/cm were used for all specimens as compromise values most frequently used by researchers in this field.

Effect of Sample Drying

In pore structure or oxygen permeability tests, samples used should be dry in order for mercury or oxygen to penetrate the pores. It is accepted that the method of drying the sample influences the pore size distribution and permeability results to some extent. The effects of three common drying procedures on cement paste were studied by Winslow and Dimond [101]. These were: equilibration over magnesium perchlorate hydrates (p drying), evacuation over a dry ice trap (D drying), and oven drying at 105°C. The methods are given in order of increasing severity of water removal. They found that the data in the coarse pore region roughly coincided, but those in diameters less than about 0.1μm, the results were found to be a direct function of the drying method. The results of oven drying were more severe than those due to D drying and P drying, both of which were nearer to each other, as shown in Figure 5.3. They concluded that small differences in the amount of residual water left in the pores are in some way responsible for change in contact angle and the relatively large changes in pore size distribution in the fine pore region, oven drying was finally selected.

Other methods of drying which are less severe than oven drying at 105°C are: vacuum drying [110] and solvent replacement [111]. In this investigation, oven-drying at 105°C for 24h was the method used for pore size distribution and permeability measurements of the different concrete mixes, on the assumption that the more complete removal of water from the sample prior to the intrusion of mercury or oxygen gas probably provides a better assessment of the actual pore spaces present.

5.3.2 Apparatus

The instrument used to measure the mercury intrusion was a Micromertics Pore Size 9320, which has a maximum pressuring capacity of 30,000 psi (206.8 MPa), shown in Figure 5.4, and mainly consists of the following parts:

- Penetrometer (the container which holds the sample),
- Two low and one high pressure ports
- Sources for generating the pressure for the low and high pressure runs.
- An instrument for controlling the applied pressure and monitoring the progress of mercury penetration.

The complete pressurization of the sample is done in two stages: a low pressure run and a high pressure run (from 1.55-206.8 MPa). These two pressurisation stages are carried

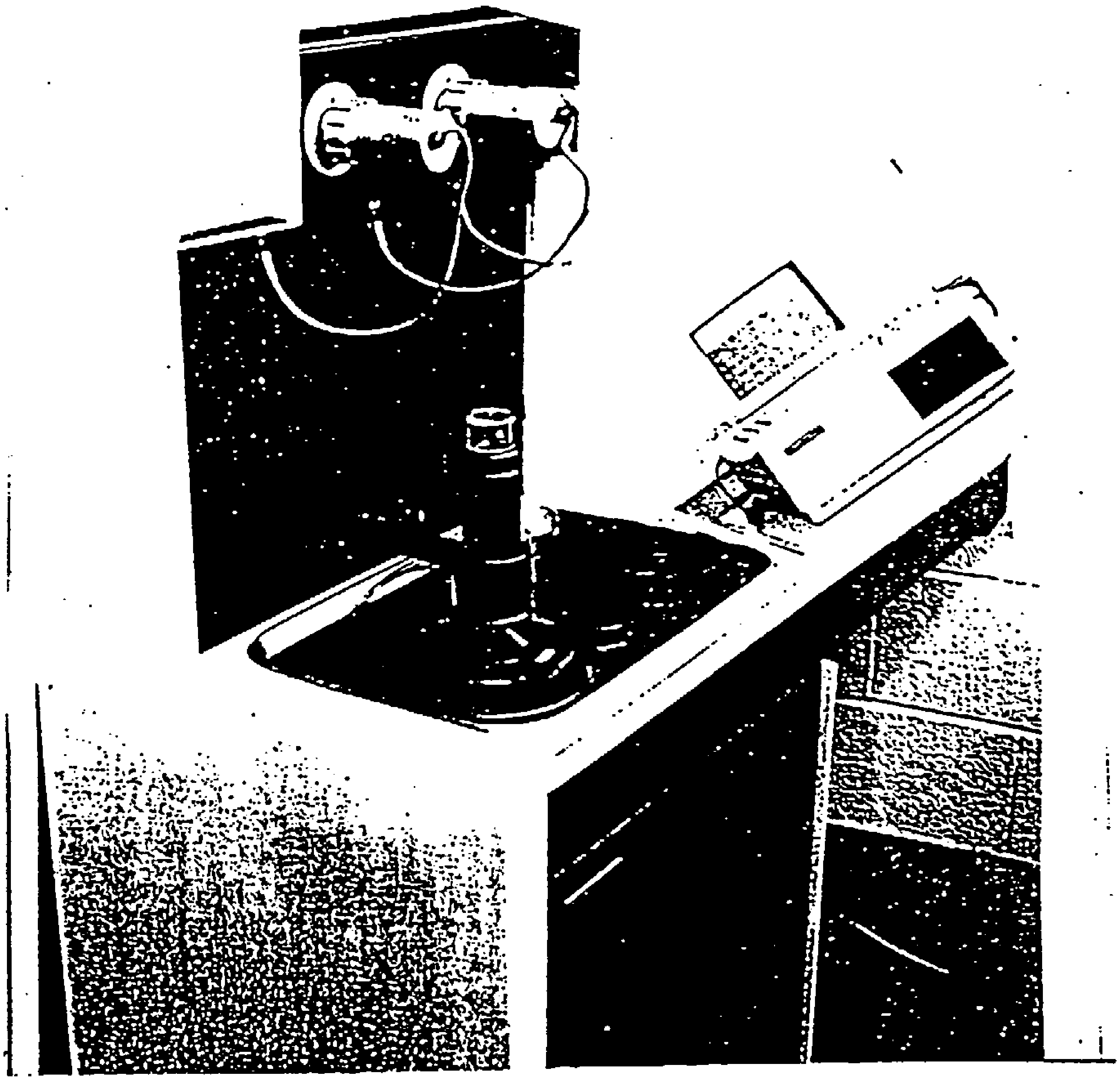


Figure 5.4 Mercury porosimeter model Micrometrics Pore Size 9320 used in this study

out in two different ports. The low pressure ports can run up to two samples, whilst the high port run only one sample. In the two low pressure ports, a dry sample is put into a penetrometer and is subjected to vacuum pressure to get rid of any air entrapped inside the sample. Mercury is then filled into the penetrometer which contains the evacuated sample (in the low pressure ports). Pressure is increased in steps and intrusion readings are measured, and then de-pressurization is carried out again to the atmospheric pressure. In the low pressure ports the penetrometer is maintained in a horizontal position during the low pressure run, thus permitting operation substantially free of any pressure applied by the weight of mercury.

For high pressure measurement the penetrometer filled with the sample and mercury is loaded into the third port and a high pressure run (up to 206.8 MPa) is gradually commenced. The run is finished when the mercury is depressurised back to the atmospheric pressure. The volume of intruded mercury that is read at each pressure step is taken by a built-in software.

When the high pressure run is completed, the data are printed automatically for each sample in a report which consists of several pages of both tabulated and plotted data with a data summary table. The data of MIP are then transferred to the computer for analysis and plotting.

5.3.3 Presentation of results

Pore size distributions are not easy to use directly, so it is acceptable to use simple parameters which represent the pore size distribution. If a standard MIP report is examined, the following information is obtained, several pages of data in spreadsheet format and data summary page that reports end results such as [112]:

Total Intrusion Volume: This is the maximum volume of mercury intruded into the sample of the highest pressure attained during analysis.

Total Pore (Surface) Area: This is the surface area within the pores determined as a function of the pressure range and is based on the assumption of cylindrical geometry.

Median Pore Distribution: Which is the pore size at 50% intrusion obtained from the cumulative intrusion curve.

Average Pore Diameter: This is the pore volume divided by the pore area assuming that all pores are right cylinders.

With the spreadsheet data, the precise intrusion volumes for each equilibrium pressure can be compared. A typical computer output on intruded pore volume and pore size distribution is presented in Table 5.2. A total of six columns of data provide full details on pore characteristics. In the first column, equilibrium pressures attained during analysis are listed (in psia). These pressures are automatically corrected for mercury head pressure when the penetrometer is in the vertical position during high pressure analysis.

The second column lists the pore diameters in micrometers (μm) for each pressure point obtained by the Washburn equation explained in section 5.3.1. The remaining four columns provide the following data for each pressure point:

- Mean pore diameter (in μm)
- Cumulative intrusion volume (in ml/g); this curve helps define pore shape, also shows the hysteresis region for the comparison of advancing and receding contact angles.
- Incremental intrusion volume (in ml/g); this curve is frequently used to indicate the amount of intrusion between two diameters.
- Differential intrusion volume by diameter (in ml/g-μm); shows intrusion values between diameters.

The experimental pore size distribution data in this work are presented in the form of the cumulative pore size distribution curves, the pore volume parameter being expressed in milliliter per ovendry gram of mortar. The volumes are accumulated from the largest diameter pore measured to the smallest, the order which pores are physically intruded by mercury. To retain the normal sense of the logarithmic scale of the abscissa, the cumulation curve proceeds from lower right to upper left, as can be seen in Figure 5.8. This type of distribution has the advantage of showing readily the total porosity, the threshold diameter and limiting pore size (i.e. pore diameter beyond which no intrusion takes place with further application of pressure). This curve also shows the median pore diameter(i.e. pore diameter which corresponds to 50% of the total intrusion volume).

Another common way of presenting the data [78,113,116], is to plot the log differential intrusion volume as a function of pore diameter; this is essentially d(volume)/d log (diameter), a typical example of which is shown in Figure 5.9. This curve shows pore size distribution, their location and volume.

Table 5.2 Typical computer output for intruded pore volume and pore structure (sample ID: ZY air curing).

Pressure psia	Pore diameter µm	Mean diameter µm	Cumulative volume ml/g	Incremental volume ml/g
2.41	75.0522	75.0522	0.0000	0.0000
19.95	9.0661	42.0591	0.0000	0.0000
52.08	3.4731	6.2696	0.0015	0.0015
102.06	1.7721	2.6226	0.0021	0.0006
207.30	0.8725	1.3223	0.0053	0.0032
354.86	0.5097	0.6911	0.0095	0.0042
499.90	0.3618	0.4357	0.0139	0.0044
697.73	0.2592	0.3105	0.0201	0.0062
996.35	0.1815	0.2204	0.0280	0.0079
1503.11	0.1203	0.1509	0.0369	0.0089
1795.35	0.1007	0.1105	0.0404	0.0035
2002.79	0.0903	0.0955	0.0423	0.0020
2506.52	0.0722	0.0812	0.0463	0.0039
2905.79	0.0622	0.0672	0.0488	0.0025
3999.98	0.0452	0.0537	0.0541	0.0053
5002.23	0.0362	0.0407	0.0572	0.0032
5999.00	0.0301	0.0332	0.0594	0.0022
7995.92	0.0226	0.0264	0.0627	0.0032
10013.69	0.0181	0.0203	0.0650	0.0023
13005.13	0.0139	0.0160	0.0673	0.0023
17990.08	0.0101	0.0120	0.0696	0.0024
19992.90	0.0090	0.0095	0.0703	0.0007
29975.84	0.0060	0.0075	0.0733	0.0030
19974.82	0.0091	0.0075	0.0733	0.0000
9982.96	0.0181	0.0136	0.0732	-0.0001
4979.32	0.0363	0.0272	0.0721	-0.0011
997.37	0.1813	0.1088	0.0638	-0.0083
499.69	0.3619	0.2716	0.0581	-0.0057

```
                    INTRUSION DATA SUMMARY

           TOTAL INTRUSION VOLUME =     0.0733 mL/g
                 TOTAL PORE AREA =      6.223 sq-m/g
MEDIAN PORE DIAMETER (VOLUME) =     0.1216 µm
  MEDIAN PORE DIAMETER (AREA) =     0.0172 µm
 AVERAGE PORE DIAMETER (4V/A) =     0.0471 µm
                    BULK DENSITY =     1.9570 g/mL
  APPARENT (SKELETAL) DENSITY =     2.2846 g/mL
                        POROSITY =      14.34 %
              STEM VOLUME USED =         45 %
```

Another method used for presenting pore size distribution data of this work is d(volume)/d(pressure) versus pore diameter [59,102]. Since the pore diameter and intrusion pressure are related reciprocally, the function dv/dp may be used instead of the direct function of the pore diameter. Nyame and Illston [102] defined "the maximum continuous pore radius" as the pore radius at which dv/dp has a maximum value. Roy and Parker [78] also determined "the maximum continuous pore radius" following this definition. However, our results show that it is difficult to determine "the maximum continuous pore radius" from dv/dp-D curves, the curve consists of one or more peaks. There is the following relationship between dv/dp and dv/dlogD [102]:

$$dv / d\log(D) = \frac{p}{2.303}\frac{dv}{dp} .$$

Obviously, dv/dlog(D) and dv/dD has a relationship.

$$dv / d\log D = 2.303D\frac{dv}{dD}$$

However, for comparison purposes the d(volume)/d(diameter) versus pore diameter plots were also used. The results show that this type of curve also show pore size distribution, their location and volume.

Pore measurements for all specimens were originally made starting from a diameter of 200μm (i.e. the figure begins at this diameter). The minimum pore diameter intruded was approximately 0.008μm.

In the results under discussion, the data will be presented for all the specimens tested in the four forms mentioned above and as histograms. The age of testing of all specimens was 240 days unless otherwise stated.

5.4 Influence of Curing Conditions

It is well known that both porosity and pore size distribution are the most important factors affecting pore structure. They have a vital influence on the properties of concrete. Generally, total porosity and closed pores are important in correlating mechanical property results, but they are less critical with regard to properties such as permeability that are associated with durability [68]. It has been suggested [77] that only relatively large pores (greater than 0.09μm) contribute to poor durability. Of course, different researchers have suggested values for this critical value of pore diameter which ranges from 0.09μm~0.15μm [73,101,117]. In this work, the pores are divided into two kinds according to whether they are above or below 0.1μm. Curing conditions are also very important for the pore structure of concrete. As mentioned before, three kinds of curing conditions were used in these experiments viz 1) air-curing; 2) 7 day water, then air-curing, and 3) continuous water-curing.

All the results are summarized in Table 5.3.

5.4.1 Porosity

Porosity is one of the major factors controlling the chemical resistivity and strength of cement pastes, mortars or concretes, its influence can be further understood by measuring the size distribution of the pores [118].

Opinion regarding meaningful techniques for porosity measurements of hydrated Portland cement paste is varied [101]. The major difficulty with most techniques is that the water residing in the pores has to be removed in order to obtain the measurement, and the removal of the water may lead to changes in the microstructure of the material [118].

Some researchers used the helium pycnometric method, while others used mercury porosimetry method (MIP) to study the porosity. In the helium pycnometric method, samples are conditioned at 11 percent RH to avoid dissociation of the hydrates (due to further removal of water on drying) prior to volume displacement with helium [119].

In this investigation MIP technique was used for measuring total porosity of several concrete systems and to compare the porosity results under different curing regimes.

The porosity of concrete is found to be influenced by the amount of cement replacement materials incorporated and by the type of curing. As seen from Table 5.3, for all mixes, the specimens cured in air posses the largest porosity, or total intrusion volume, compared to those continuously cured in water and those subjected to 7 days water/air-curing. The continuously water cured specimens have the smallest porosity and total intrusion volume. These results show that curing conditions affect the porosity of concretes both with and without replacement materials.

The intrusion pore volume of control mix W cured in air is 0.053 ml/g and the corresponding value are 0.0392 ml/g and 0.0488ml/g for the specimens cured in water

Table 5.3 Influence of curing on porosity and pore volume of large and small pores

Mix	Curing condition	Porosity (%)	Intruded pore volume (ml/g)			Pores (%)	
			Total pore volume	Large pores >0.1μm	Small pores >0.1μm	Large	Small
W	Wet	8.67	0.0392	0.0074	0.0318	18.88	81.12
W	7d wet/air	11.21	0.0488	0.0164	0.0324	33.60	66.40
W	Air	11.42	0.0530	0.0160	0.0370	30.19	69.81
X	Wet	9.90	0.0478	0.0099	0.0379	20.71	79.29
X	7d wet/air	11.30	0.0545	0.0167	0.0378	30.64	69.36
X	Air	14.16	0.0672	0.0322	0.0350	47.92	52.08
Y	Wet	11.04	0.0540	0.0087	0.0453	16.11	83.89
Y	7d wet/air	11.72	0.0581	0.0186	0.0395	32.01	67.99
Y	Air	15.17	0.0732	0.0425	0.0307	58.06	41.94
Z	Wet	7.75	0.0372	0.0087	0.0285	23.39	76.61
Z	7d wet/air	9.00	0.0433	0.0126	0.0307	29.10	70.90
Z	Air	14.61	0.0702	0.0399	0.0303	56.84	43.16
ZX	7d wet/air	10.76	0.0546	0.0189	0.0357	34.62	65.38
ZX	Air	15.10	0.0767	0.0384	0.0383	50.06	49.94
ZY	Wet	4.95	0.0319	0.0080	0.0239	25.08	74.92
ZY	7d wet/air	8.07	0.0396	0.0141	0.0255	35.61	64.39
ZY	Air	14.34	0.0733	0.0404	0.0329	55.12	44.88

* Age of concrete specimens at testing = 240 days

and 7d water/air-curing respectively. Similar results were obtained in all other mixes containing replacement materials as shown in Figure 5.5.

The porosity results showed significant differences for the water-cured specimens. It can be seen that porosity values for slag/SF specimens (4.95-7.75%) were lower than control and FA/SF specimens (8.67-11.04%). This is understandable, because at relatively large cement replacement levels by pozzolanic/cementious materials, sufficient water should be available to continue the release of lime arising from Portland cement hydration to react with the siliceous addition, and the water requirement was satisfied. As expected, porosity decreased by increasing the amount of slag/SF in the mixes. Concrete with 165kg/m^3 slag gave smaller porosity than mixes with 80 and 125kg/m^3 slag replacement. This can be related to the development of hydration product which fills the pores and reduces the total porosity. Also this shows the importance of continuous water-curing and the influence of slag/SF additives in filling the pores.

On the other hand the 80 kg/m^3 FA/SF wet-cured specimens large pores proportion was about the same as of the slag/SF mixes and comparable with that of control mix . This shows the advantage of continuos wet curing on large pores reduction.

However, continuous water-curing produces the smallest porosity for all concretes with and without replacement materials. This general observation is entirely in accord with ordinary expectation. Because enough water during the whole hydration process is essential for the formation of hydration products of cement and pozzolanic materials. The interparticle space gradually decreases as the volume of hydration products increases. The more the extent of hydration, the less is the interparticle space and the smaller is the porosity.

Air-curing condition is the worst and leads to produce the largest porosity due to the insufficient water available for the hydration of cement and pozzolanic materials. It is known that the hydration products of cement grain are in general significantly finer in particle size than the original cement grains. Therefore the insufficient hydration of cement and pozzolanic materials contribute to the development of the large porosity.

With the exclusion of control air-cured specimens, the porosities of FA/SF and slag/SF specimens were found to lie in the range between (14.16-15.17%). The control air-cured specimens showed lower porosity (11.42%). This high porosity of FA/SF and slag/SF indicates the need for larger amounts of water to continue the reaction. The increase in porosity and pore volume (Table 5.3) reported later are direct results of the slowing and possible stoppage, of the pozzolanic/cementious activities of cement replacements. Such increases could effect the permeability and loss of durability with time.

However, concrete with replacemental materials seems to be more sensitive to air drying conditions compared with concrete without replacement materials, therefore more water-curing is essential for concrete with replacement materials.

7 days water/air-curing condition gives porosity values between those corresponding to porosity for continuous water and air-curing. It should be noted that porosities under 7 days water/air-curing are much less than the corresponding value under air-curing for concrete with replacement materials. From the results, it can be seen that porosity difference is diminished between control and FA/SF mixes when 7 day water-curing was provided, and for slag/SF 7d wet/air-cured specimens the porosity was found lower than the corresponding control mix. The porosity values were 11.42, 11.30, 11.72, 9.0, 10.76 and 8.07% for mixes W, X, Y, Z, ZX and ZY, respectively. These results show that water-curing in the early age of concrete is more important for concrete with replacement materials than for concrete without replacement materials.

5.4.2 Threshold Diameter

The concept of "threshold diameter" measured by MIP is very important to properties, in particular, to permeability, and it refers to the pore diameter at which primary maximum intrusion occurs [102]. Studies of pore size distributions of hardened cement paste [73,77,117] generally indicate the existence of a threshold diameter. In the case of concrete, the intrusion curve of mercury exhibits a clear threshold at which large quantities of mercury first penetrate. The threshold diameter is interpreted as the minimum diameter of pores which is generally continuous throughout all regions of the hydrated cement paste [77,117] or is interpreted as a critical swelling radius at which the larger pores are filled [101]. The threshold diameter in this investigation is as shown in Figure 5.8 via the turning point of the intrusion curve; above this point there is comparatively little intrusion into the paste, and immediately below the greatest portion of the intrusion commences. The threshold diameter of control and different mineral admixture concretes is presented in Table 5.4. The effect of wet, 7d wet/air and air-curing conditions and cement replacement material will be investigated through the discussion of various sections of this chapter. The decrease of the previously defined threshold diameter with water-curing is documented in this table.

However, the following observations can be made upon examining the data and the general form and appearance of the curves which are shown in the series of figures 5.5-5.31.

1. The general distribution shifts to the right curve with increasing drying, that is the pores become increasingly coarser with prolonged drying. Significant differences are noted in the value of the specimens under the air-curing.

2. The threshold diameter in continuously wet curing decreases with increasing the FA/SF and slag/SF content, the smallest value was obtained by the 165kg/m^3 slag mix. This general observation is expected, because in wet curing one expects the interparticle spaces present within the fixed volume of hardened paste to decrease as the content of hydration products increase with increasing moisture.

3. Under the air-curing both the total intruded pore space and the threshold diameter are significantly larger for the 165kg/m^3 slag mix than for the corresponding 125kg/m^3 slag mix. The threshold diameter increases with increasing cement replacement materials, because the hydration products occupy less volume than that occupied in wet or 7d wet/air-curing.

4. The pattern of decrease in 7d wet/air-curing is similar between concrete mixes with the exception of mix Z, but the threshold diameters are larger for a given mix than under wet curing condition.

Table 5.4 Threshold Diameter of concrete mixes (μm)

Mix, kg/m^3/Curing	Wet	7d wet/air	Air
350 OPC (W)	0.08	0.1	0.27
300 OPC + 20 SF + 30 FA(X)	0.055	0.1	0.50
250 OPC + 20 SF + 80 FA (Y)	0.055	0.1	0.7
250 OPC + 20 SF + 80 slag (Z)	0.040	0.05	0.7
300 OPC + 25 SF + 125 slag (ZX)	-	0.105	0.45
250 OPC + 35 SF + 165 slag (ZY)	0.020	0.1	1.5

5.4.3 Pore Size Distribution

Although total porosity and closed pores are important parameters which affect mechanical properties, they are less critical with regard to properties such as permeability [68]. On the other hand the pore size distribution of specimens can correlate the durability of concrete at least at qualitative analysis. The results of pore size distribution of control, FA/SF and slag/SF concrete mixes are summarized in the following series of Figures 5.7-5.31.

A comparison of cumulative intrusion volume vs pore diameter for control mix at three kinds of curing conditions is given in Figure 5.8 - 5.11 The log differential intrusion volume vs pore diameter of the same samples is plotted in Figure 5.9. As seen for Figure 5.9 the coarser pore structures of the air-cured specimens and 7d wet/air-cured specimens are apparent compared to the specimens cured in water. The "threshold diameter" is 0.08μm for the specimen cured is water. For 7d wet/air-curing, and air-curing, "the threshold diameter" are 0.1μm and 0.27μm respectively. These results show that the curing conditions also have an important effect on the pore size distribution. From Table 5.3, it is seen that above 0.1μm pore volume is 0.0074ml/g for water-curing specimens.

For the 7d wet/air-curing and air-curing conditions above 0.1μm pore volume were achieved to be 0.0164 ml/g and 0.016 ml/g.

Figures 5.12 to 5.15 give a comparison of pore size distribution of mix X at different curing conditions. As mentioned before, in this mix, 20kg/m^3 SF and 30kg/m^3 FA were used as the partial replacement material of Portland cement. As seen from Figures 5.12 to 5.15, under three kinds of curing conditions, the pore size distribution of the specimens differ to a large extent. There is much more above 0.1μm pore volume in specimens cured in air and 7d wet/air, compared to the specimens cured in water. The large pore (greater than 0.1μm) volumes are 0.0167 ml/g and 0.0322 ml/g respectively for 7d wet/air-curing and air-curing. This value, however is only 0.0099 ml/g for water-curing. The specimen cured in water also has a smaller "threshold diameter", 0.055μm. For the specimens cured in air this value is 0.50μm, and 0.1μm for the specimens cured in 7d wet/air. The water-curing improved the pore structures significantly. Under continuous water-curing, concrete has good pore structures, lower porosity and less large pore volume.

Figures 5.16 to 5.19 have shown the effects of curing condition on the pore size distribution of mix Y specimens in which 20 kg/m^3 SF and 80kg/m^3 FA were used as partial replacement materials. The results same as mix X were obtained for mix Y. The large pore volume is 0.0425 ml/g for air-curing, and 0.0186 ml/g for 7d wet/air-curing. The specimen cured in water has the lowest large pore volume, 0.087 ml/g. Both air and 7d wet/air-cured specimens have a larger pore volume, compared with the specimens cured in water. The threshold diameters were also affected by the curing conditions very much. As seen from Figure 5.16, the threshold diameters are 0.055μm, 0.1μm and 0.7μm for continuous water-curing, 7d wet/air- curing and air-curing respectively. These results show that the pore size distribution is very sensitive to curing conditions for mix Y which contained more FA. Absence of water when FA particles start hydrating would result in low quality concrete which can lead to higher rates of ingress of harmful substances such as chlorides.

The cumulative intrusion volume versus pore diameter curves for the mix Z, which contained 20kg/m^3 SF and 80kg/m^3 slag as partial replacement materials, are given in Figure 5.20. The air-cured specimens have a much higher large pore volume than those of both 7d wet/air-curing and water-curing, which is 0.0399 ml/g, compared with 0.0087ml/g for water-curing and 0.0126ml/g for 7d wet/air-curing. Although there is a difference between large pore volumes of both 7d wet/air-curing and water-curing, this difference is much smaller, compared with the difference between them and air-curing. A similar effect on threshold diameters is also found. As seen from Figure 5.20 the corresponding threshold diameters are 0.04μm, 0.05μm and 0.7μm for continuous water, 7d wet/air and air-curing conditions, respectively. This result implies that water- curing at an early stage for concrete mix Z has an important role on the improvement of pore structure, and that slag/SF replacement can bring real benefits when 7 days water-curing occurs. Strength and other properties results confirmed this point.

Figures 5.24 shows the effect of 7d wet/air- and air- curing conditions on pore size distribution for mix ZX which contained 300kg/m^3 cement, 25kg/m^3 SF and 125kg/m^3 slag. As seen from Table 5.3 the specimens under air-curing have a larger pore volume, twice as much as the corresponding value under 7d wet/air-curing condition. A similar effect on threshold diameter is also found. As seen from Figure 5.24 the threshold diameter is 0.45μm for the specimens under air-curing condition and 0.105μm for the specimen under 7d wet/air-curing. In other words, air drying without water-curing produced significant coarseness in pore size distribution.

Figures 5.28 to 5.31 presents the results of pore size distribution of mix ZY which contained 250kg/m^3 OPC, 35kg/m^3 SF and 165kg/m^3 slag under different curing conditions. Apparently the curing conditions affected the pore size distribution of concrete containing slag to a great extent. The total intruded pore volume for specimens under air-curing condition is almost doubled, compared with specimens cured both in water and 7d wet/air-curing. The large pore volume are 0.008ml/g, 0.0141ml/g and 0.0404 ml/g for water-curing, 7d wet/air-curing and air-curing as seen from Table 5.3. For the specimens under air-curing condition this value is about 5 times that of the corresponding values for continuous water-curing condition. Similarly, the threshold diameter for the air-condition specimens also increased greatly, compared with water-curing and water/air-curing specimens. As seen from Table 5.4, the threshold diameters are 0.02 μm, 0.1μm and 1.5μm for water-curing, 7d wet/air-curing and air-curing respectively. The coarseness of pores is very apparent for air-curing. It should be noted that although the specimens cured under 7d wet/air-curing have coarser pores than specimens under water-curing, it has much more finer pores than the specimens under air-curing. The results indicate that continued exposure to a drying environment of inadequately cured slag/SF concrete can adversely effect its microstructure properties and thus its long-term durability. The results also show that 7 days wet-curing could be adequate for low slag/SF replacement levels, but longer wet-curing for concrete with a high slag/SF replacement level is required.

It could be concluded from the above mentioned results that specimens under continuous water-curing have better pore structures, smaller porosity, smaller threshold diameter and less large pore volume for the concrete specimens both with and without replacement materials, and a coarser pore structure was observed under air-curing for all specimens. This is because the hydrated product of cement and pozzolanic materials occupied the larger space of cement and pozzolanic particle, and filled the interparticle pores, and insufficient hydration of cementitious materials will lead to coarser pore structures due to less hydrate products.

5.5 Influence of Cement Replacement Materials on pore structure

One of the important properties of pozzolans when used as replacement materials for portland cement, is to improve the pore structure which is associated with permeability and the durability properties of concrete. Davis et al [59] indicated that pozzolans are most effective in lean mixes in reducing permeability. Mehta [120] found that at various stages during the curing process it is the volume of large pores with a diameter greater than 0.1μm not the total porosity of the hydrated paste, which is inversely

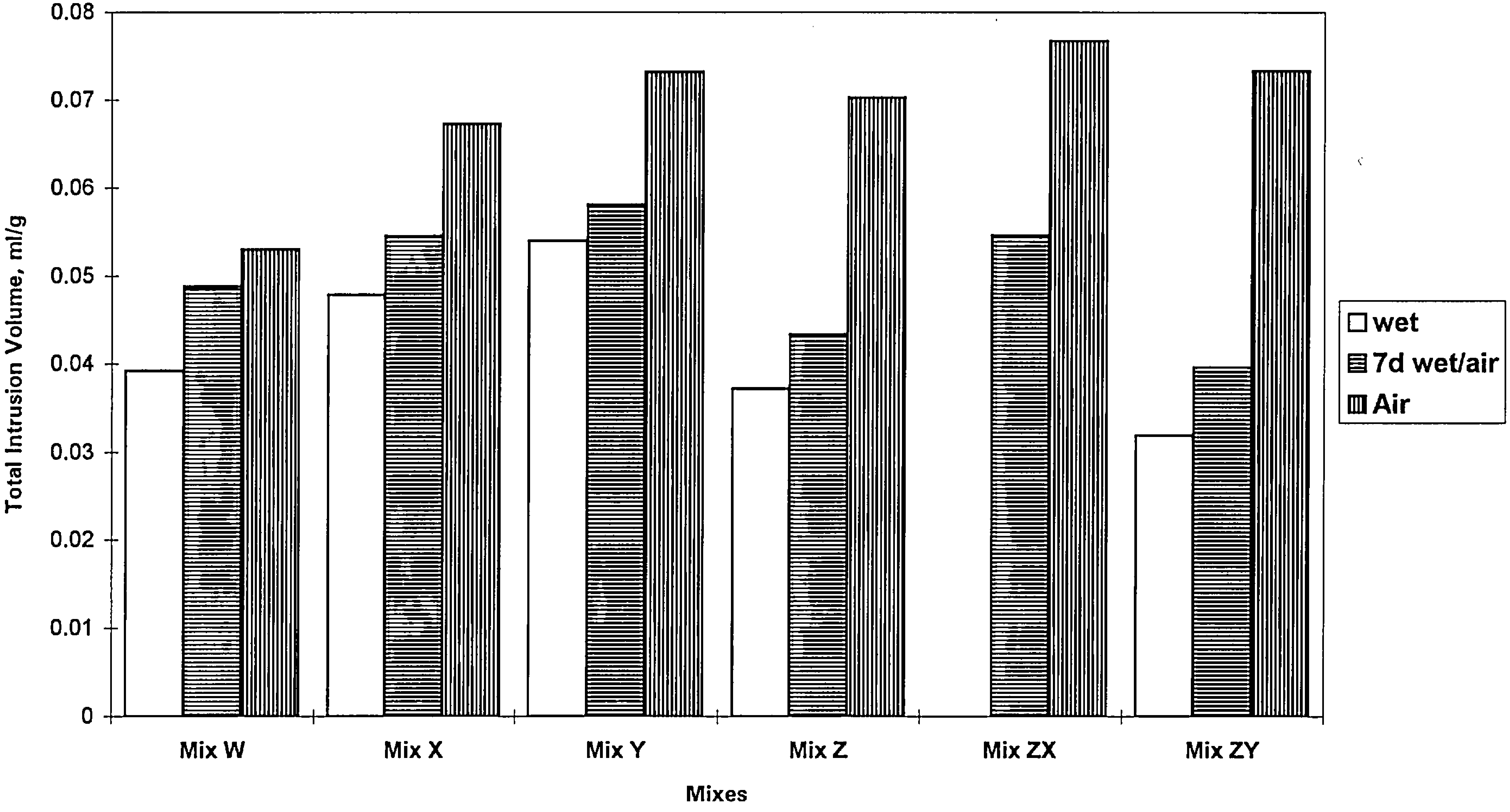


Fig 5.5 Total intrusion volume of various mixes at different curing conditions

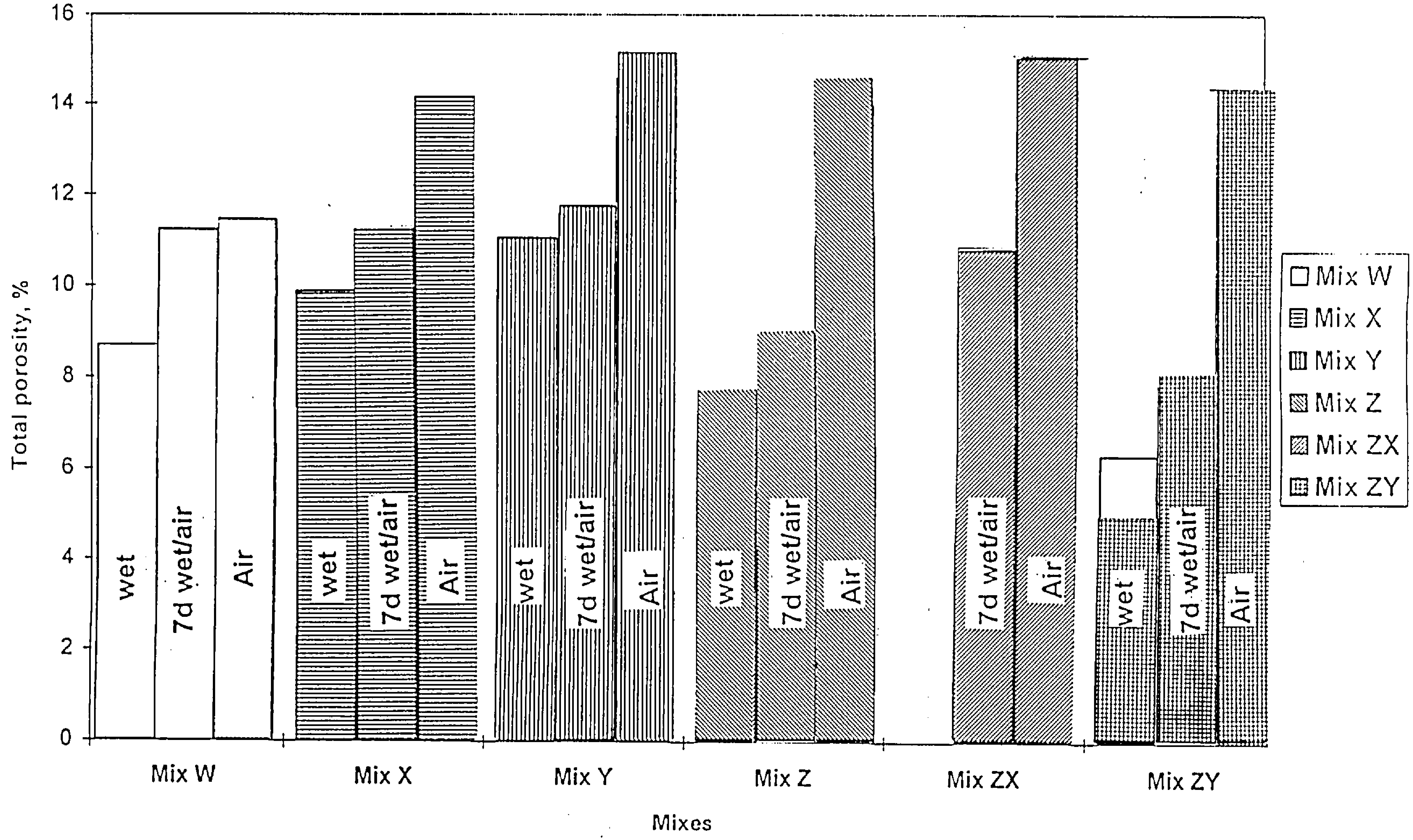


Figure 5.6 Influence of curing conditions and cement replacement materials on total porosity

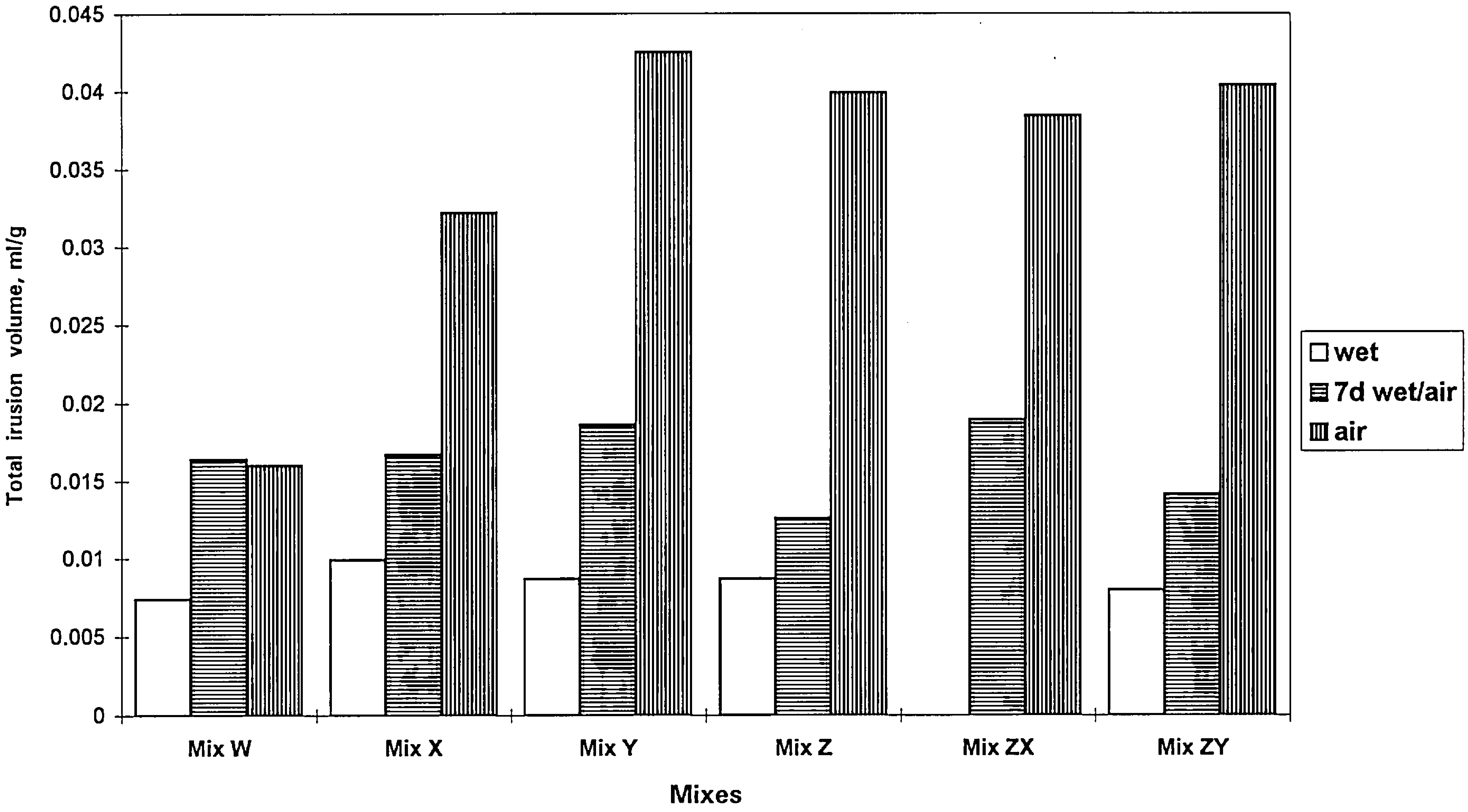


Figure 5.7 Large pore volume of various mixes at different curing conditions

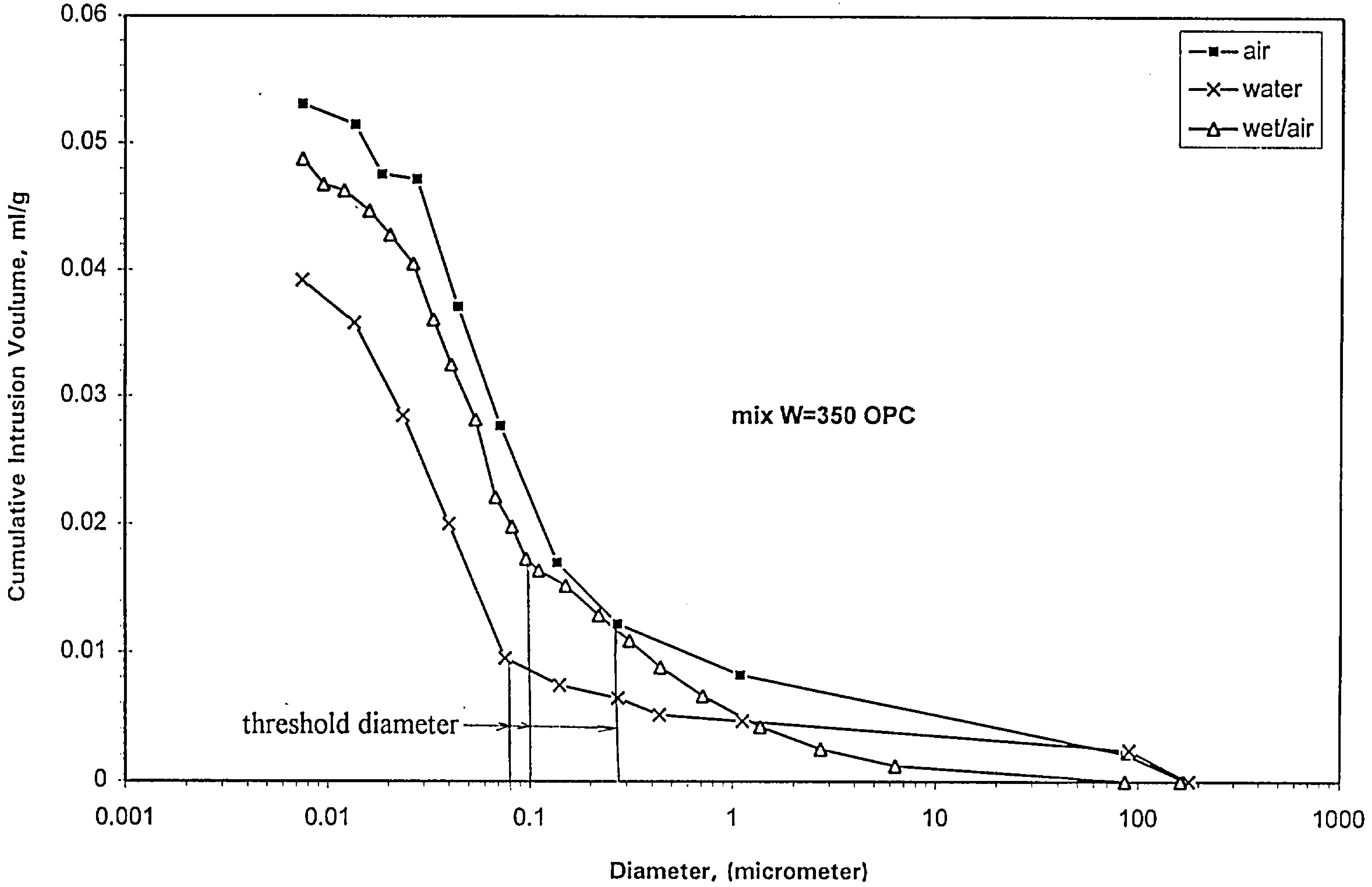


Figure 5.8 Pore size distribution at various curing conditions for mix W

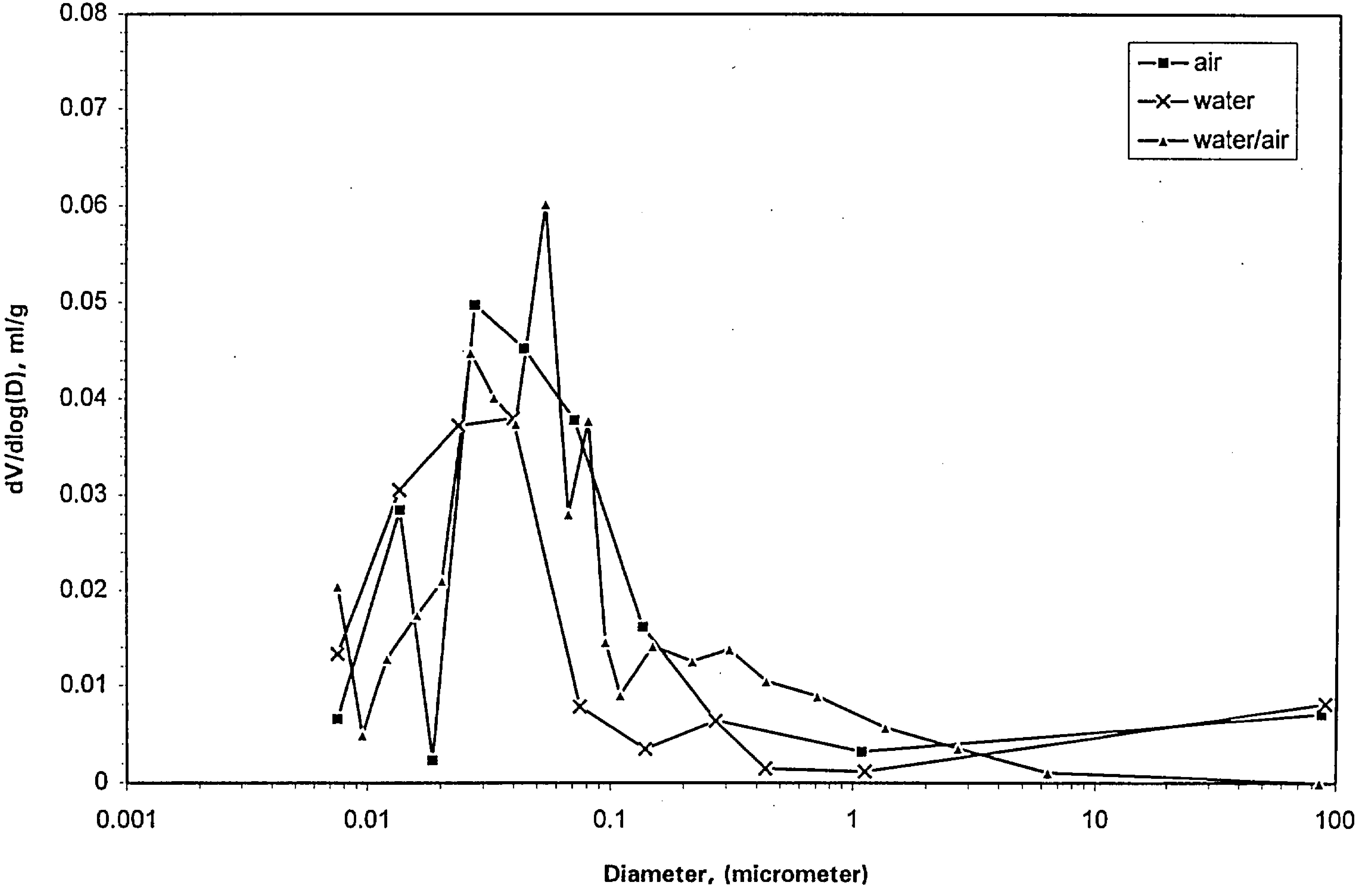


Figure 5.9 Differential pore size distribution at various curing condtions for mix W

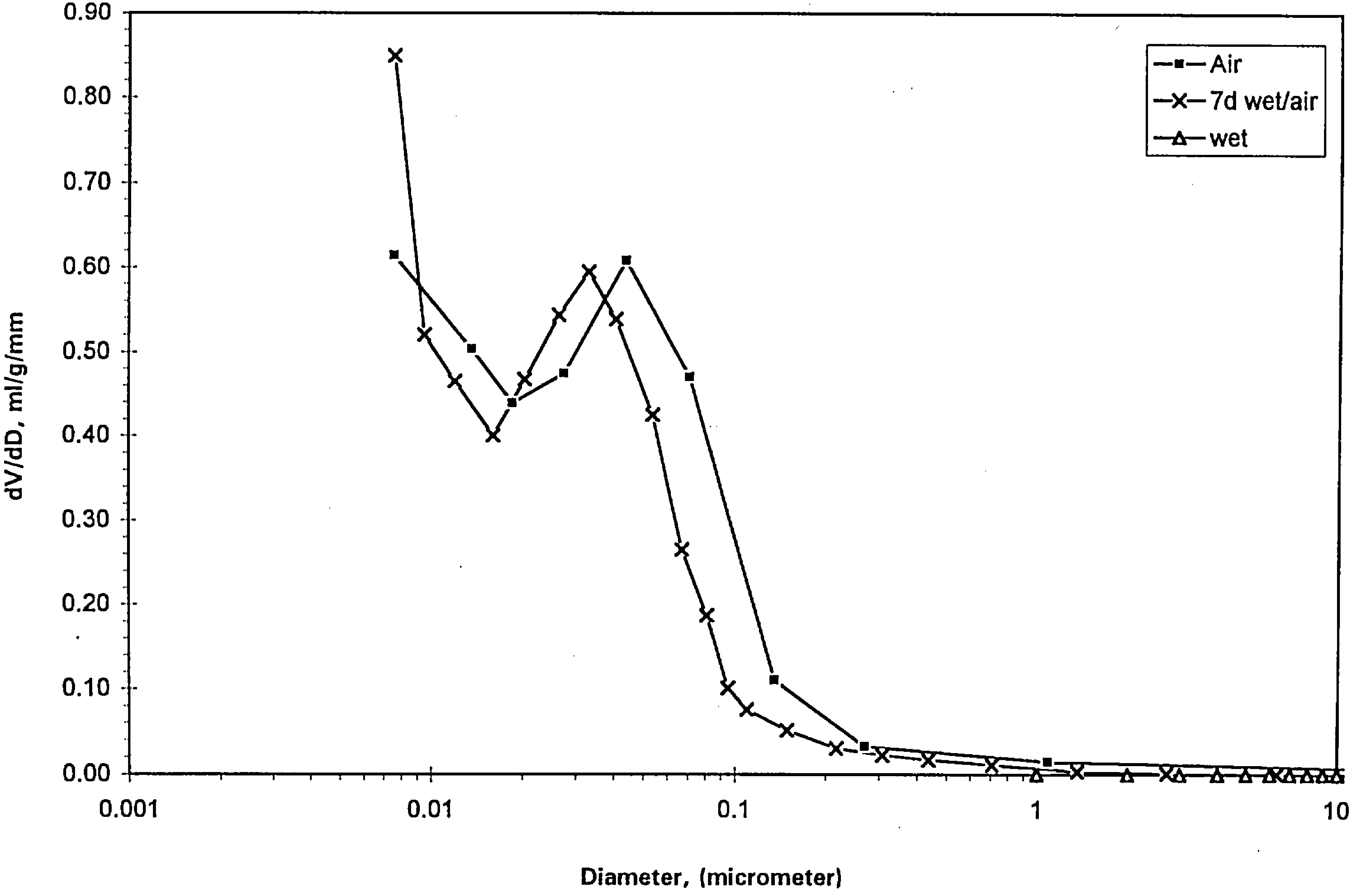


Figure 5.10 dV/dD versus D curves at different curing conditions for mix W

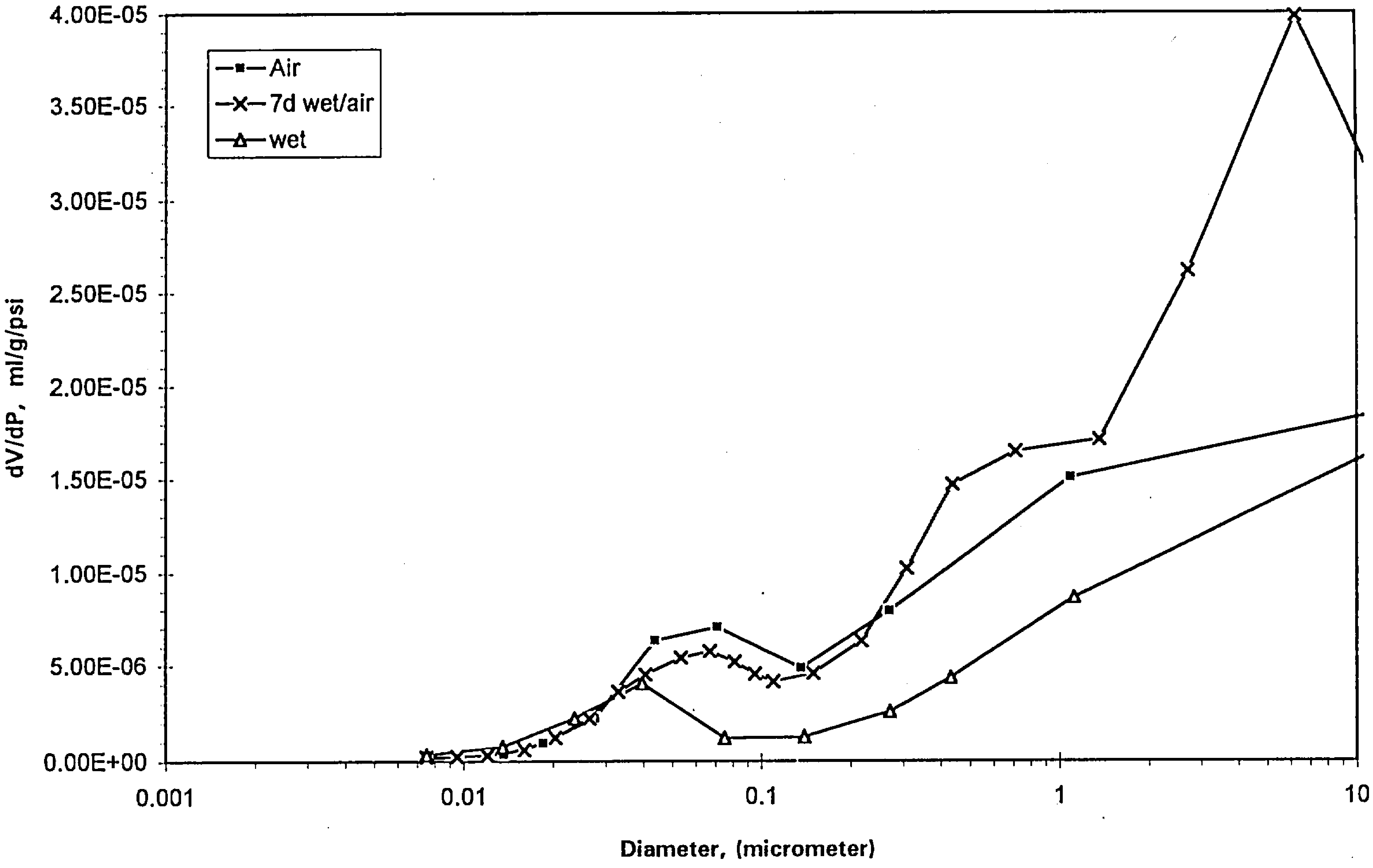


Figure 5.11 Variation of dV/dP with pore diameter for mix W

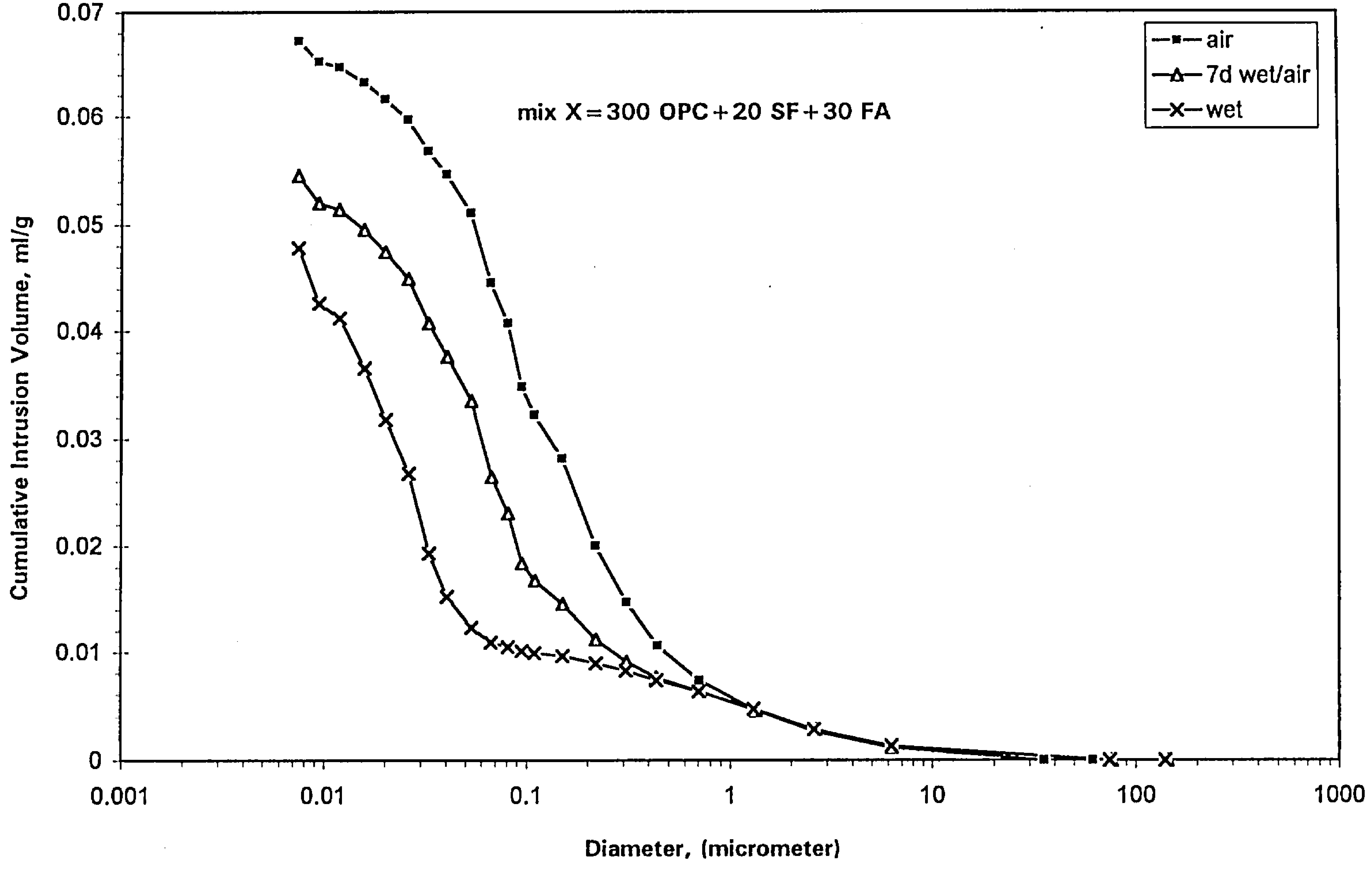


Figure 5.12 Pore size distribution at various curing conditions for mix X

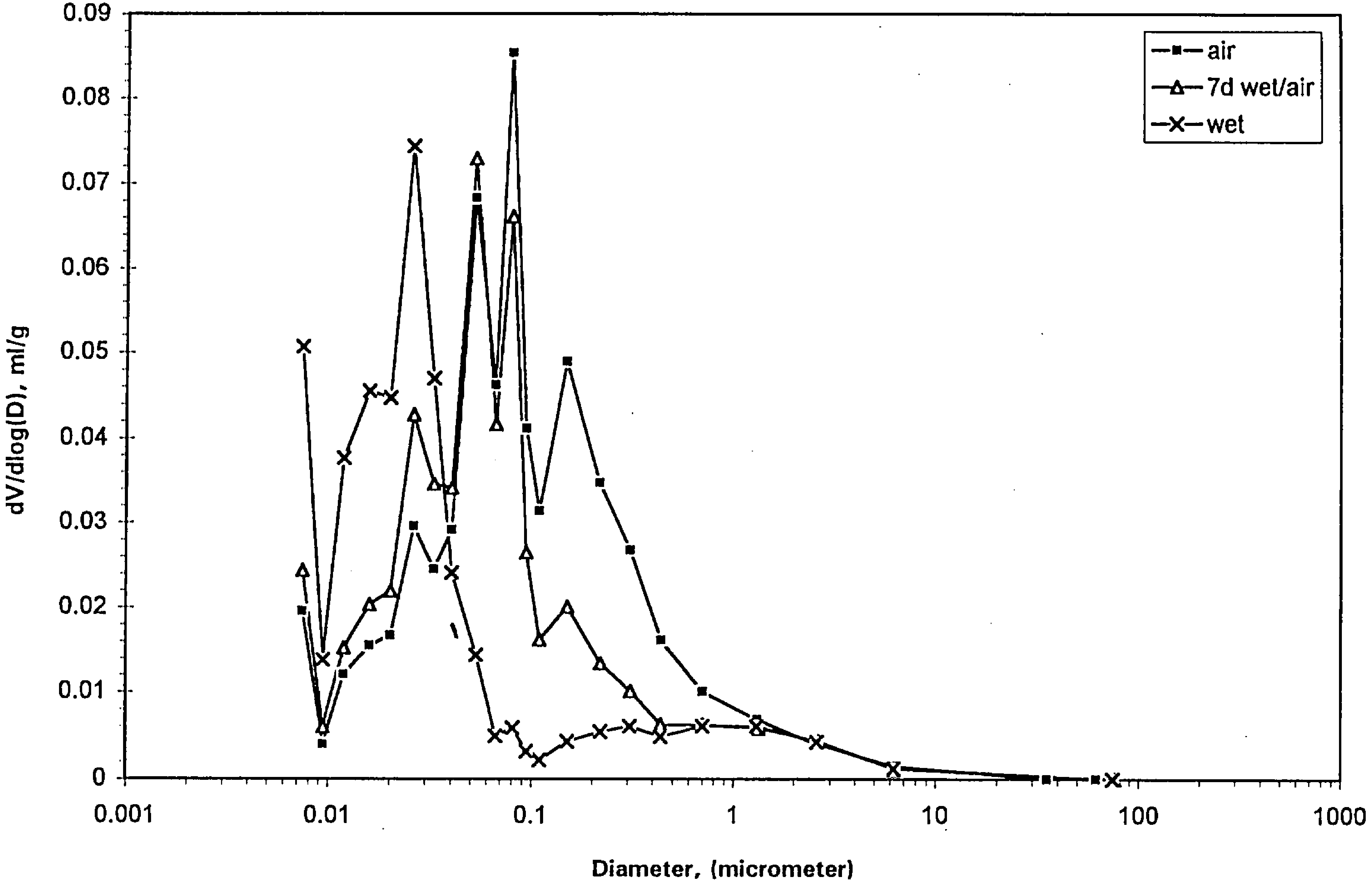


Figure 5.13 Diffrential pore size distribution at various curing conditions for mix X

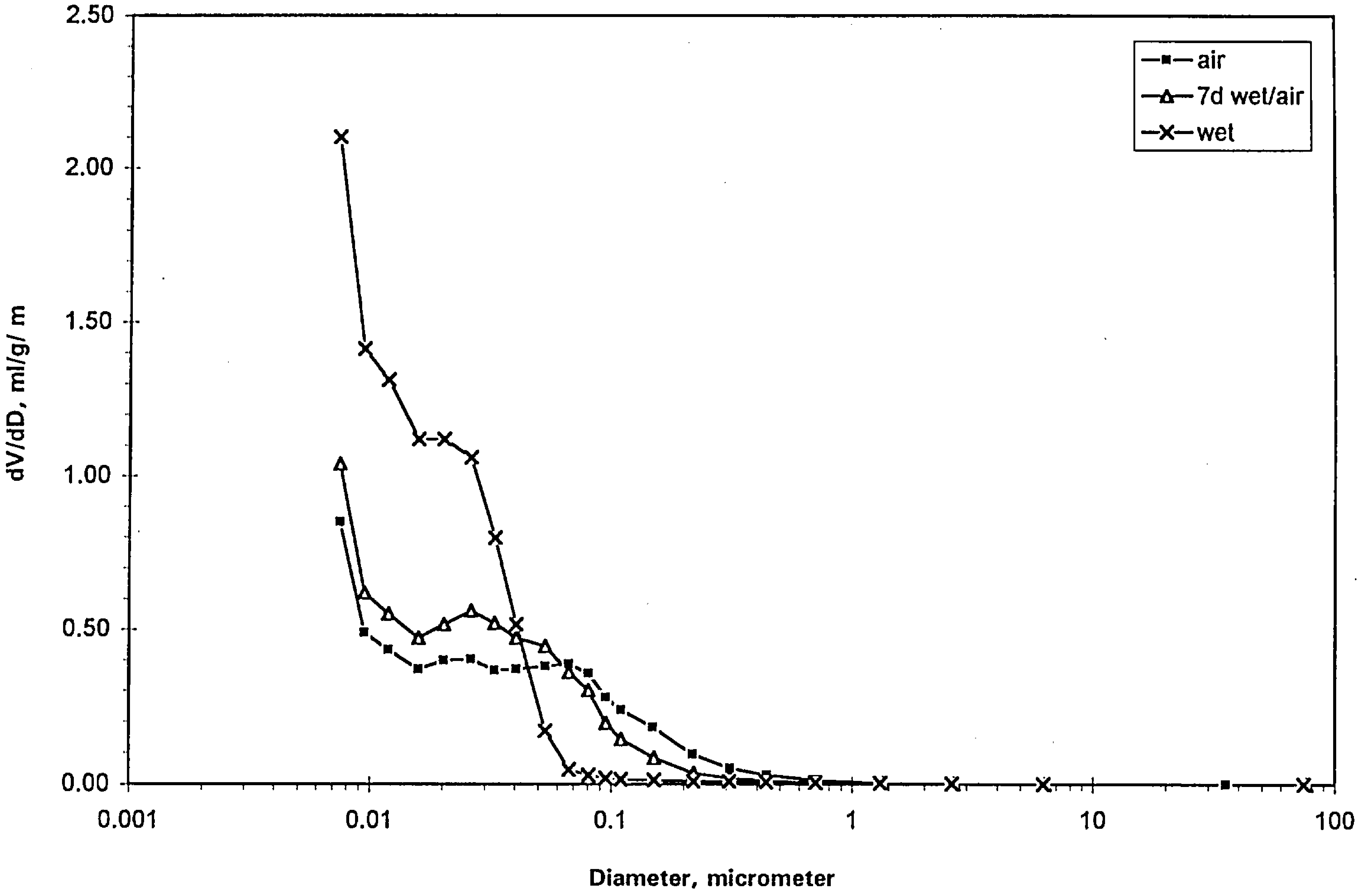


Figure 5.14 dV/dD vs. D at various curing conditions for mix X

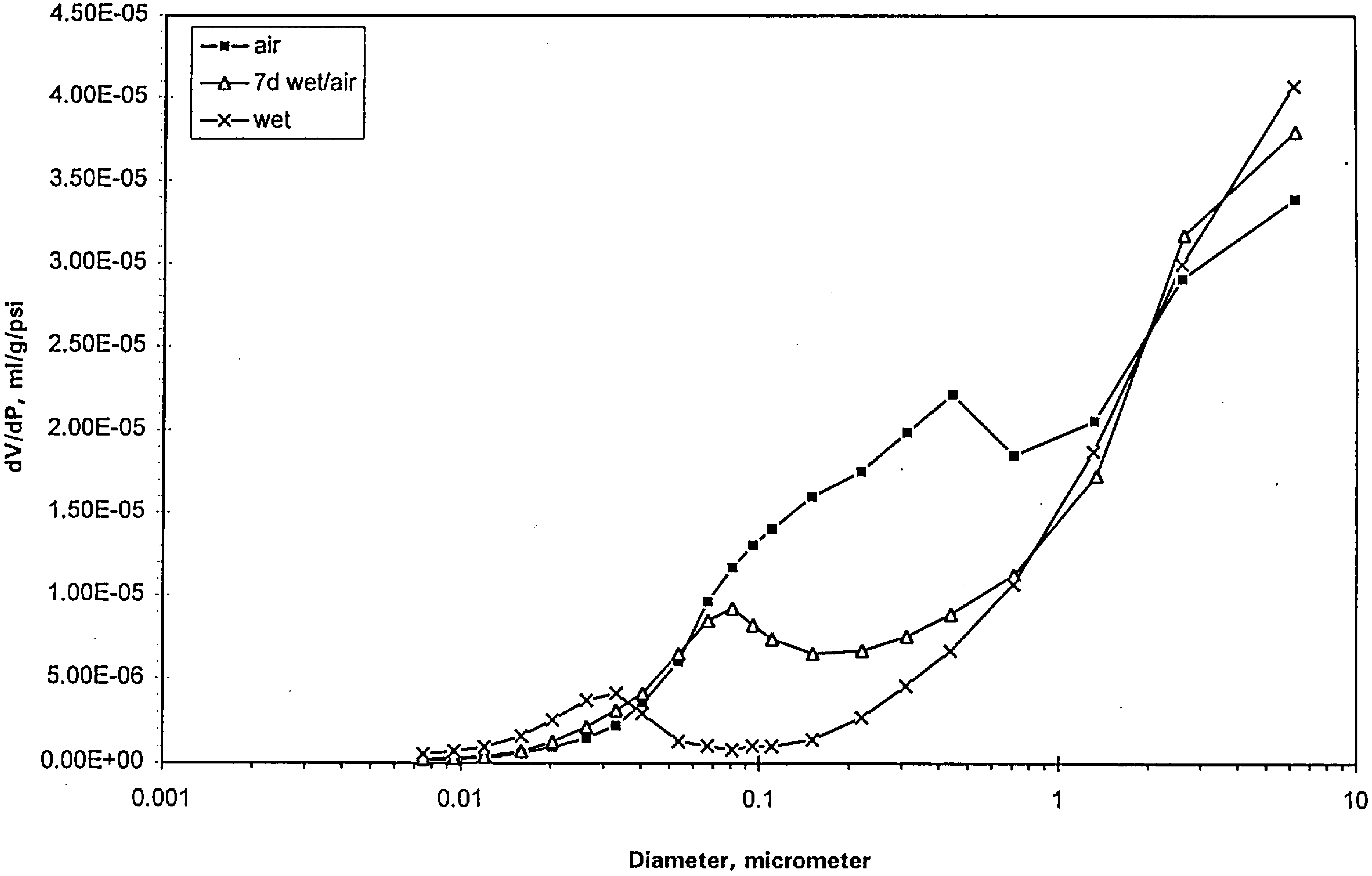


Figure 5.15 Variation of dV/dP with pore diameter for mix X

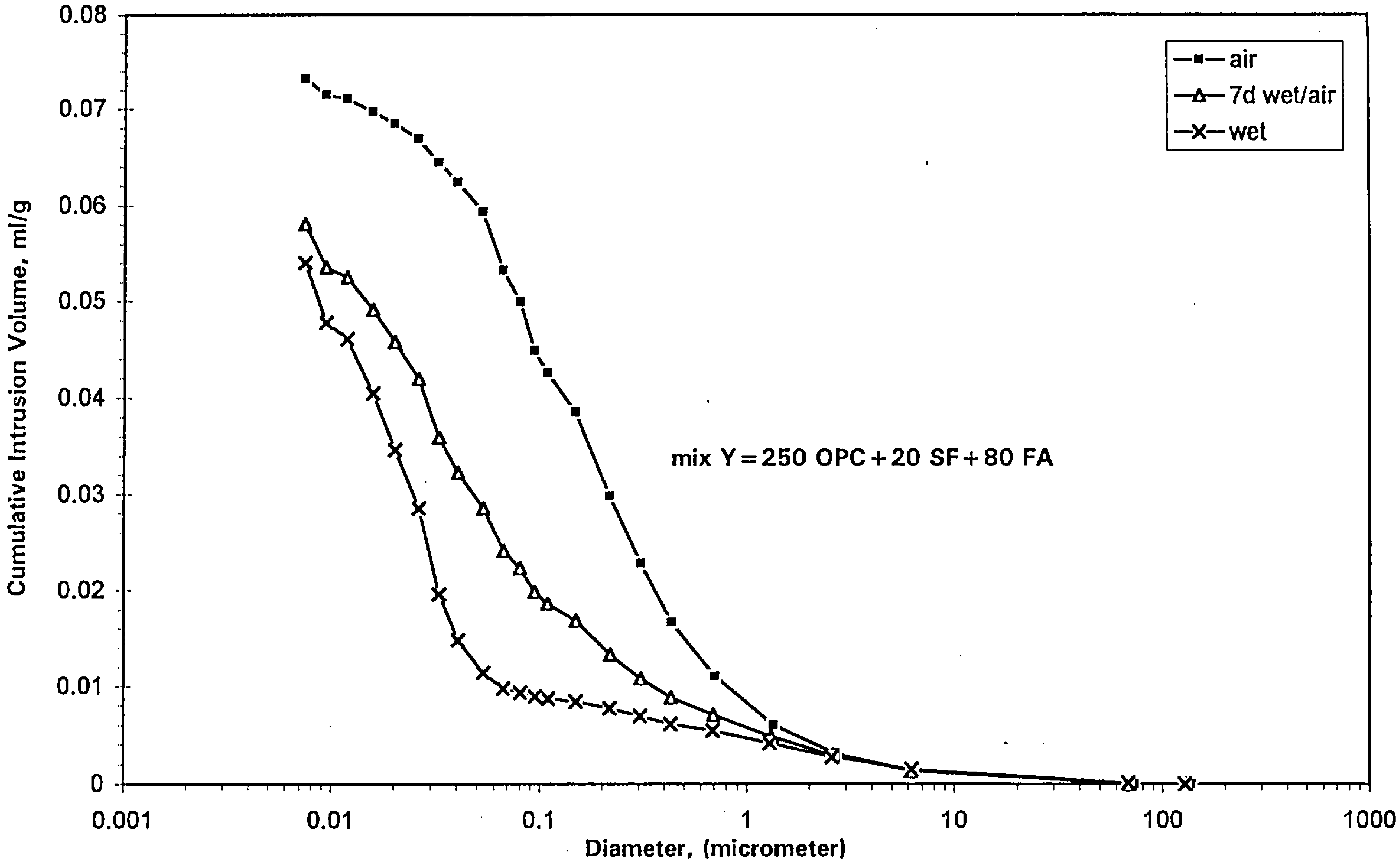


Figure 5.16 Pore size distribution at various curing conditions for mix Y

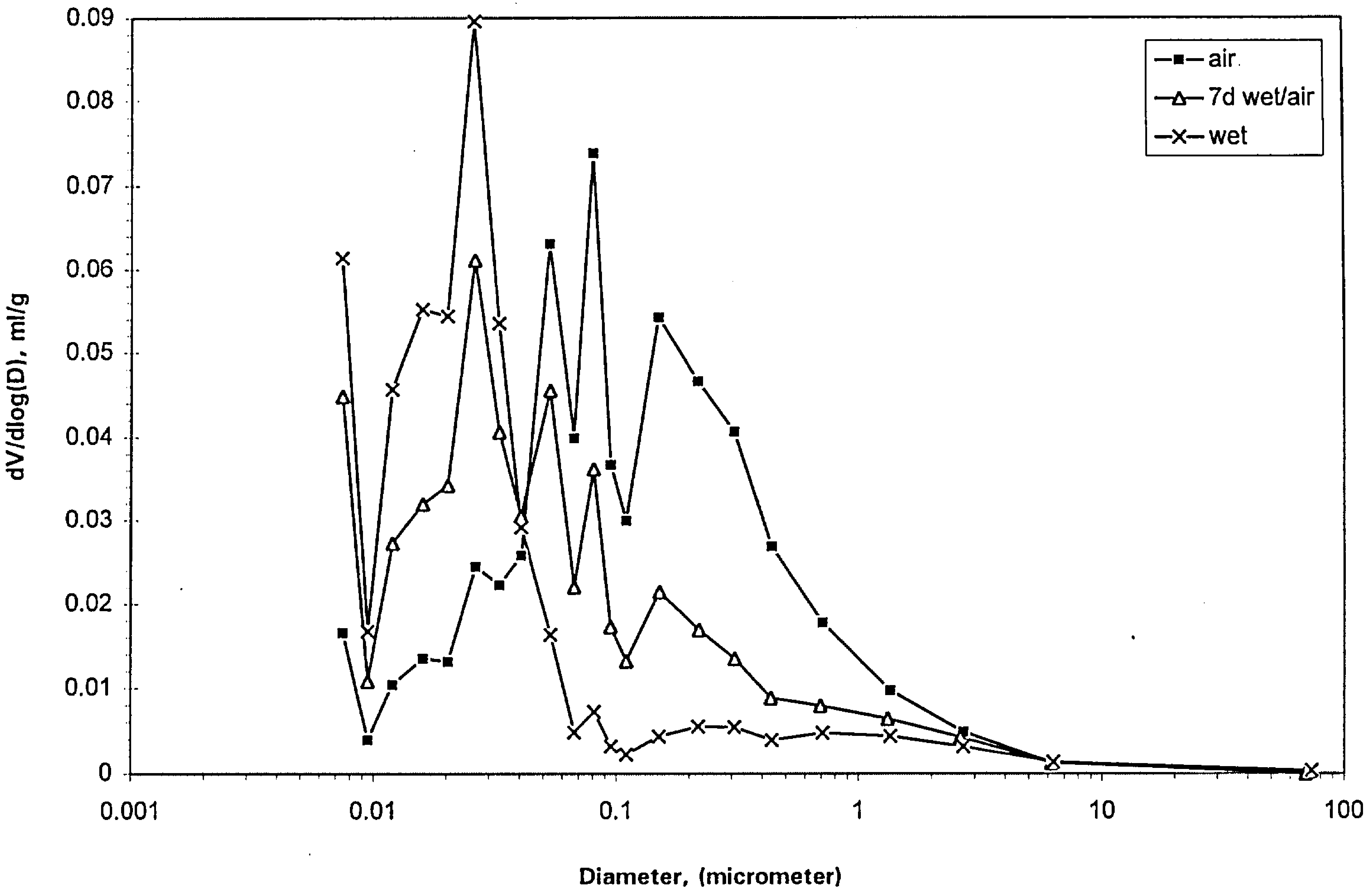


Figure 5.17 Differential pore size distribution at various curing conditions for mix Y

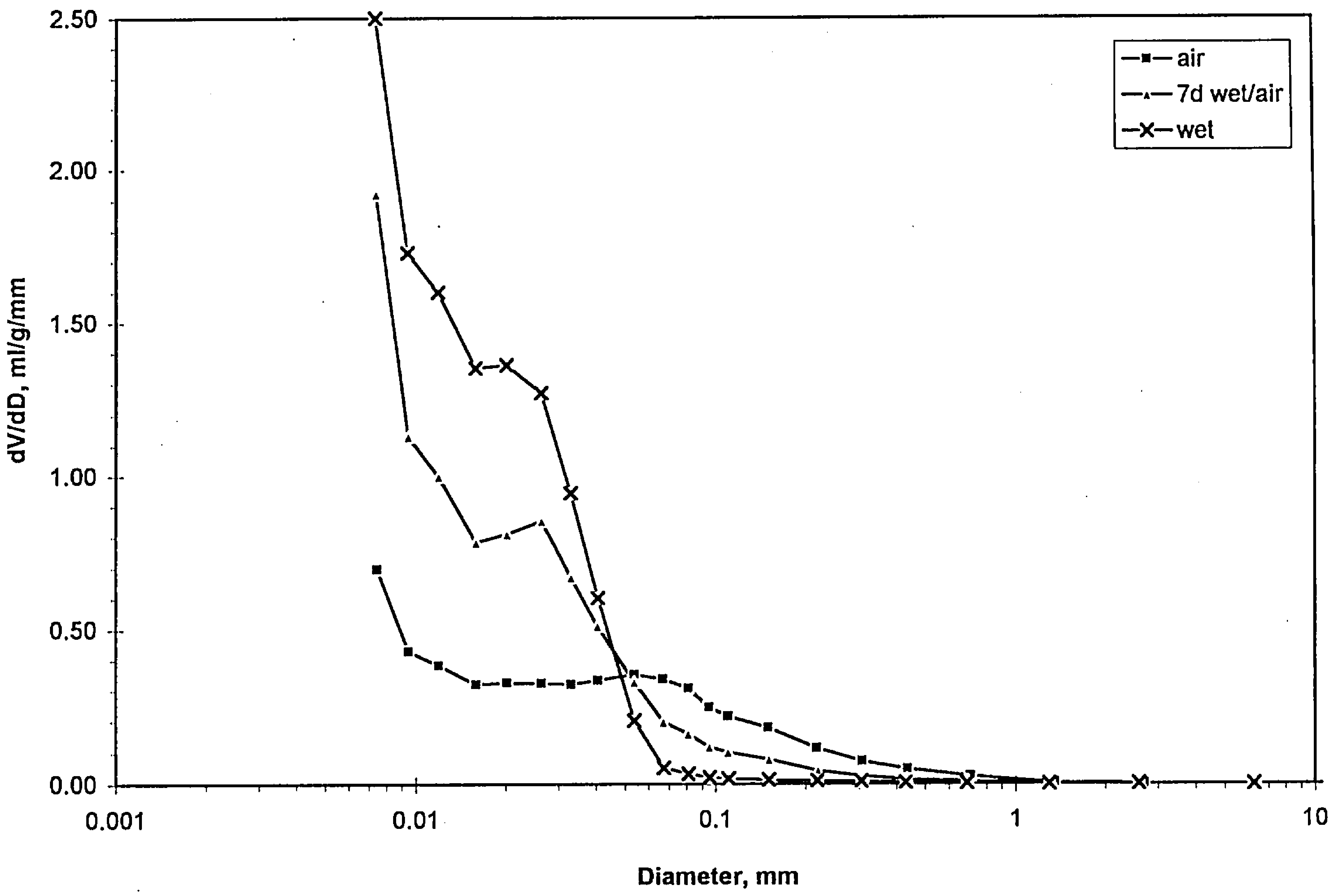


Figure 5.18 dV/dD vs. D curves at various curing conditions for mix Y

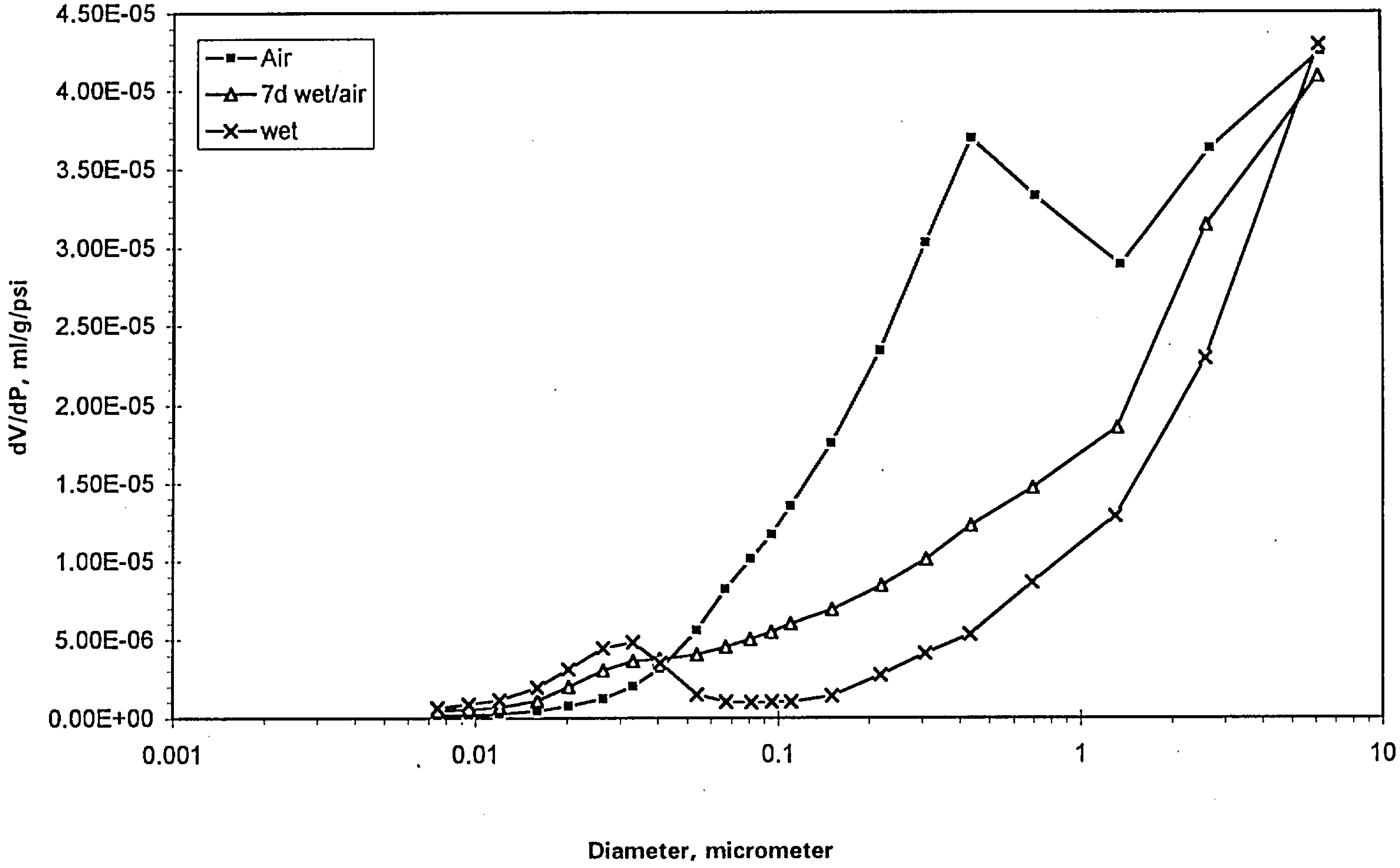


Figure 5.19 Variation of dV/dP with pore diameter for mix Y

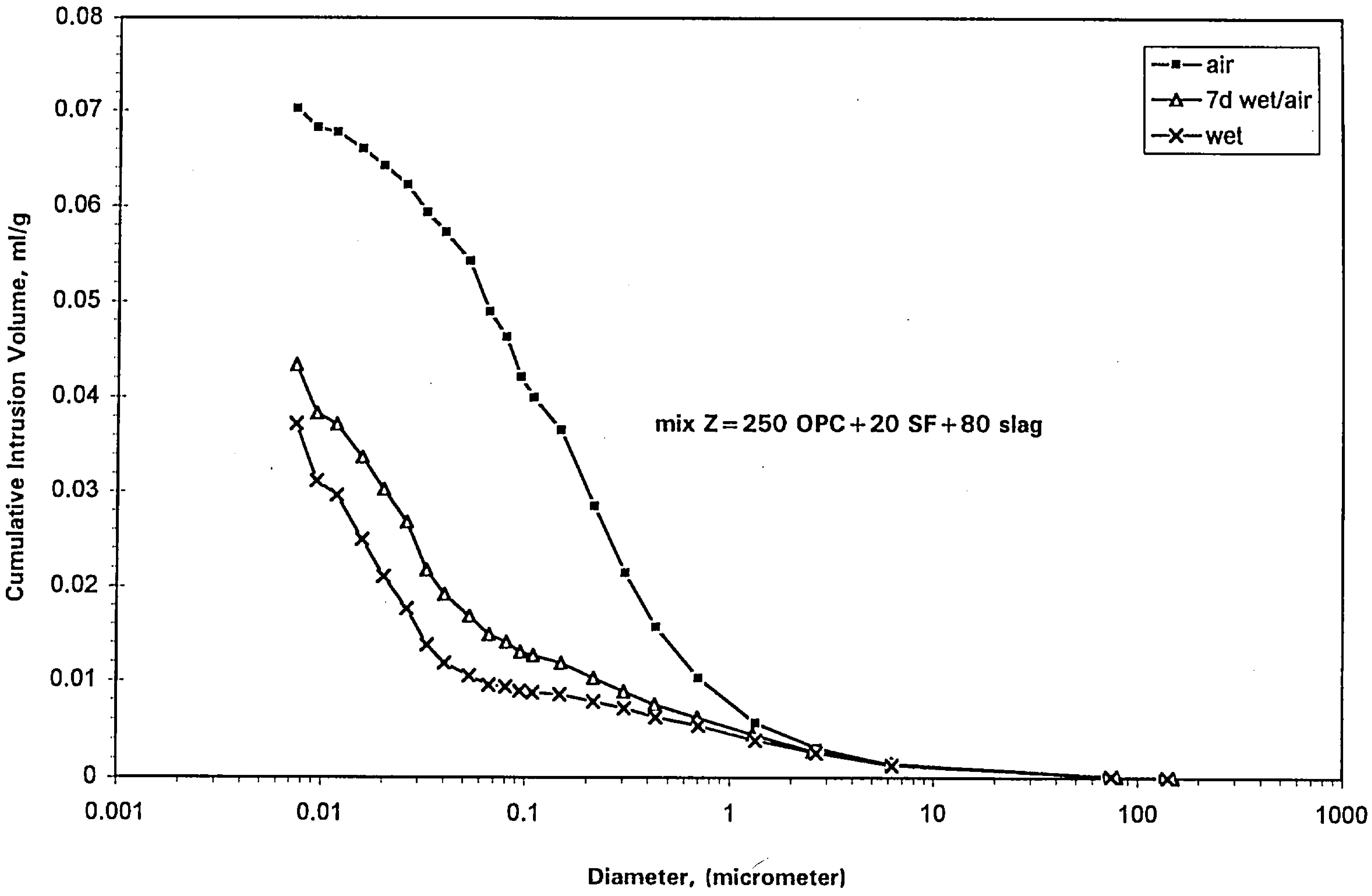


Figure 5.20 Pore size distribution at various curing conditions for mix Z

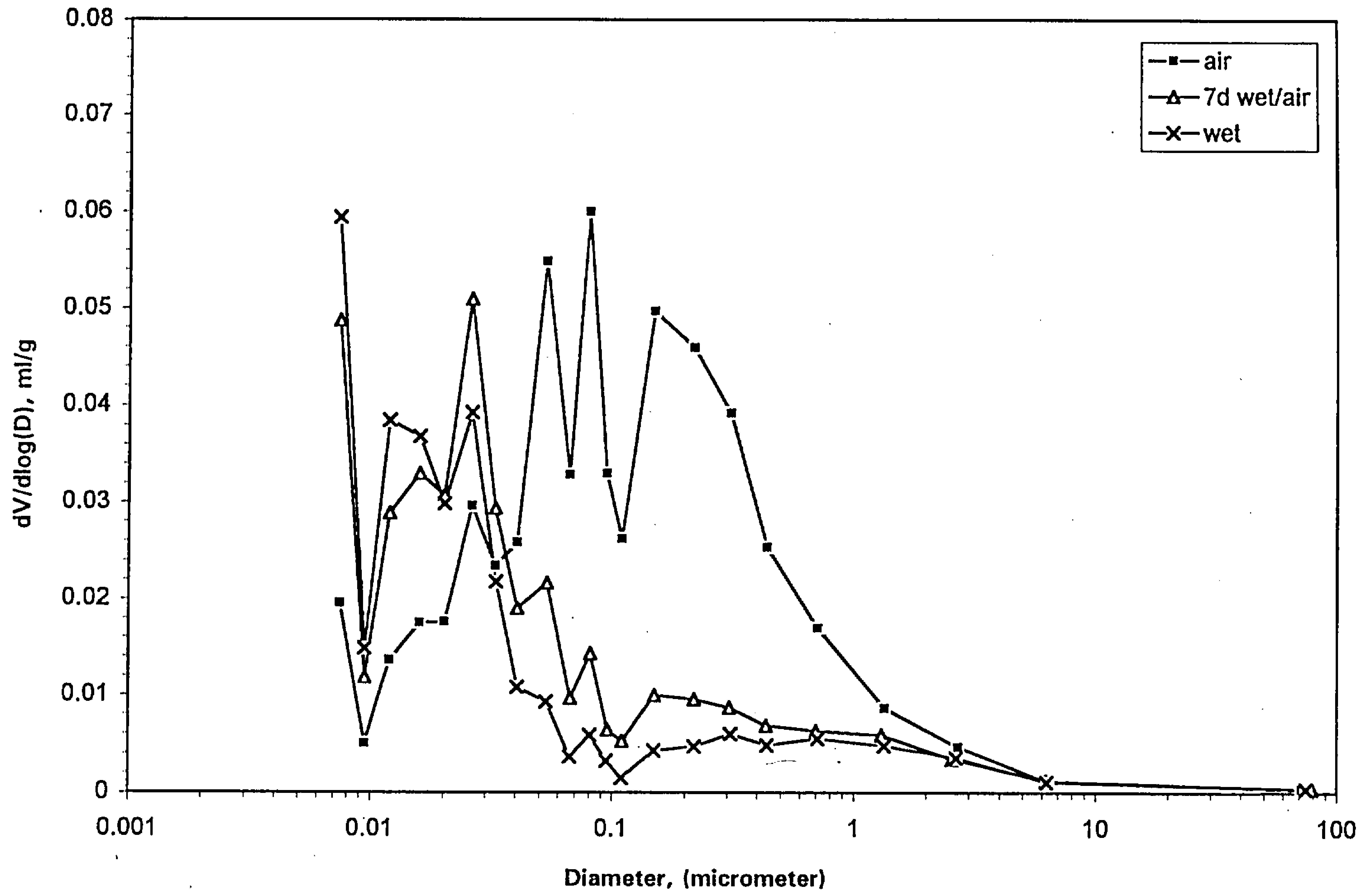


Figure 5.21 Differential pore size distribution at various curing conditions mix Z

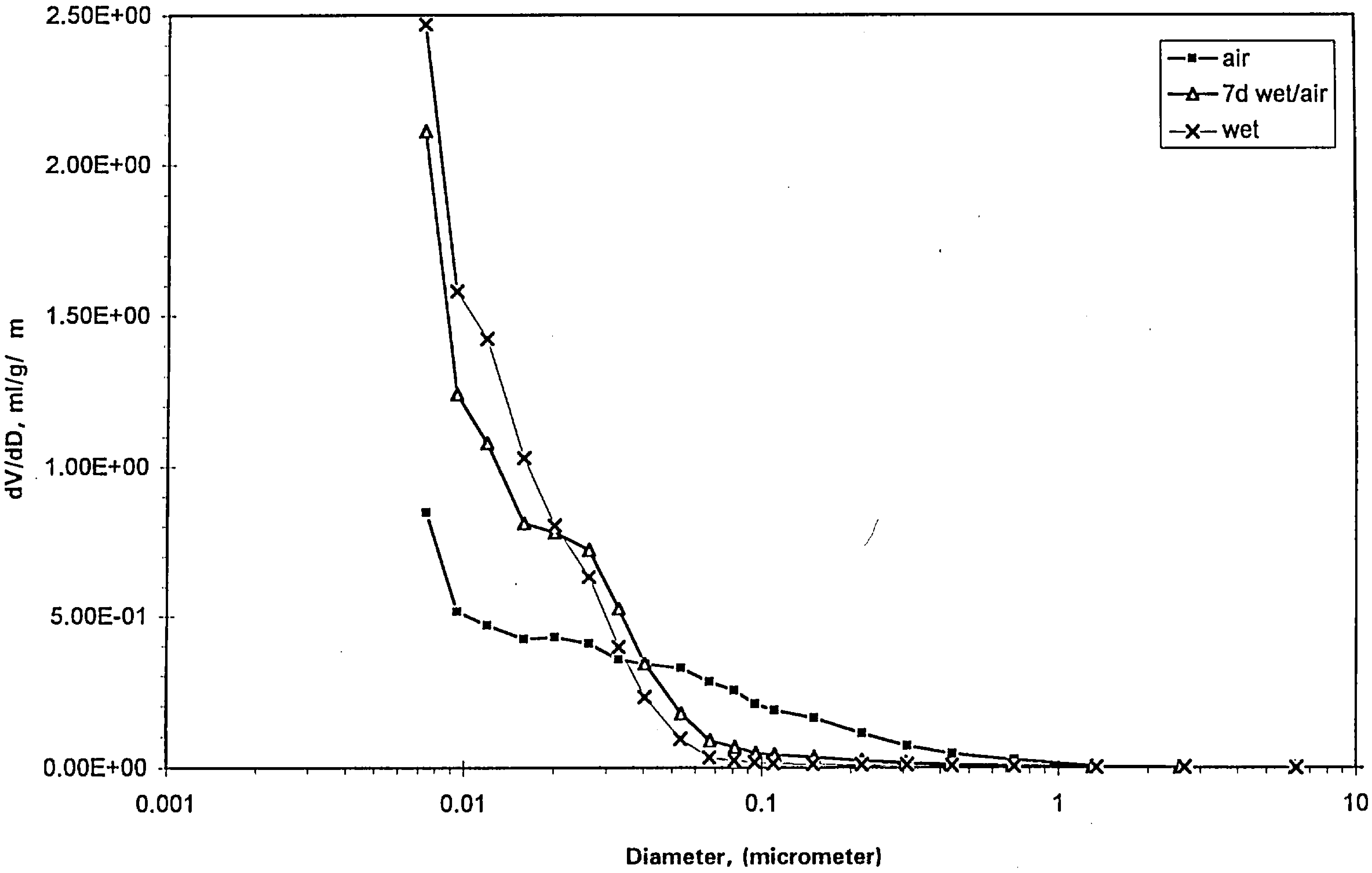


Figure 5.22 dv/dD vs. D curves at varios curing conditions for mix Z

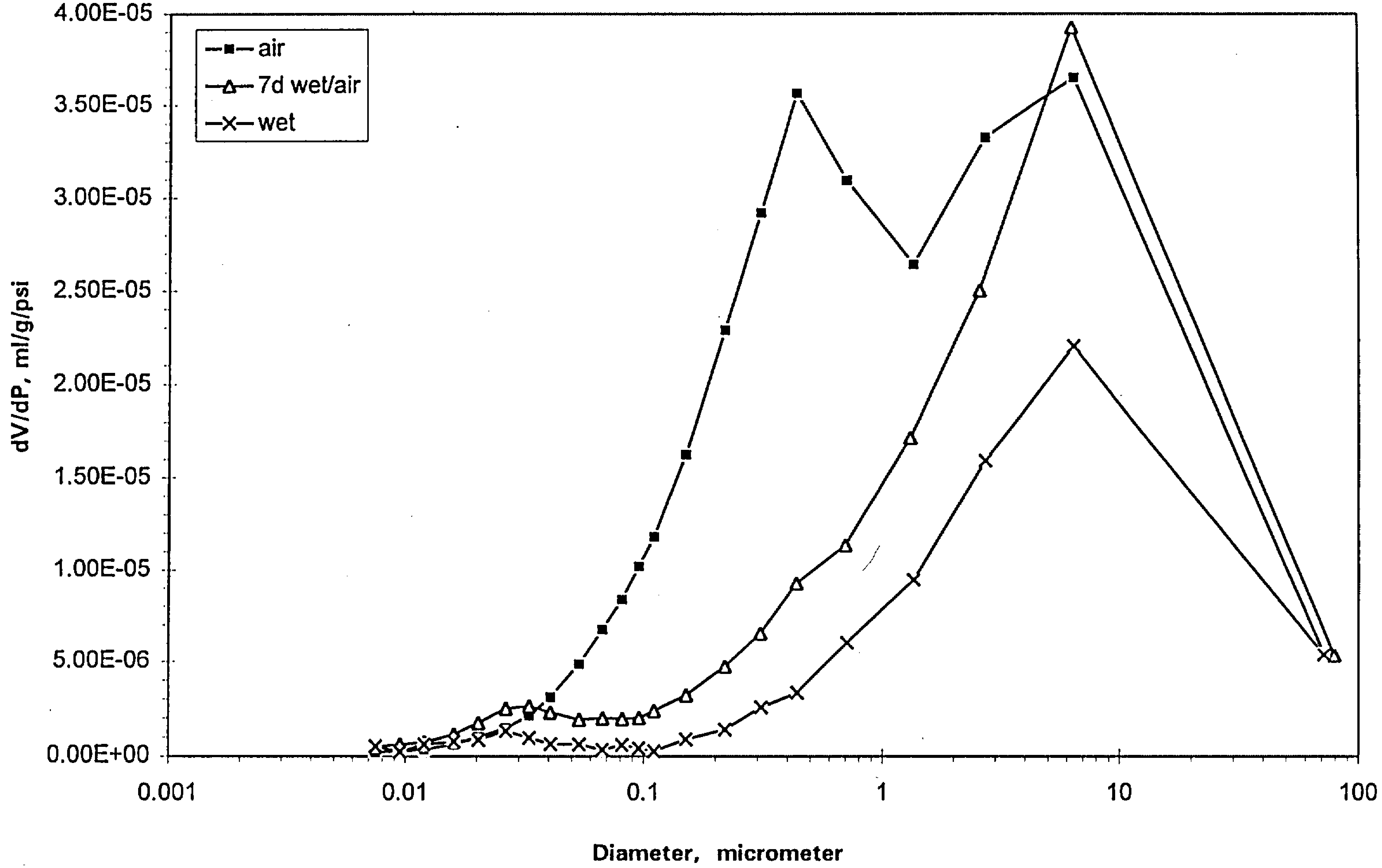


Figure 5.23 Variation of dV/dP with pore diameter for mix Z

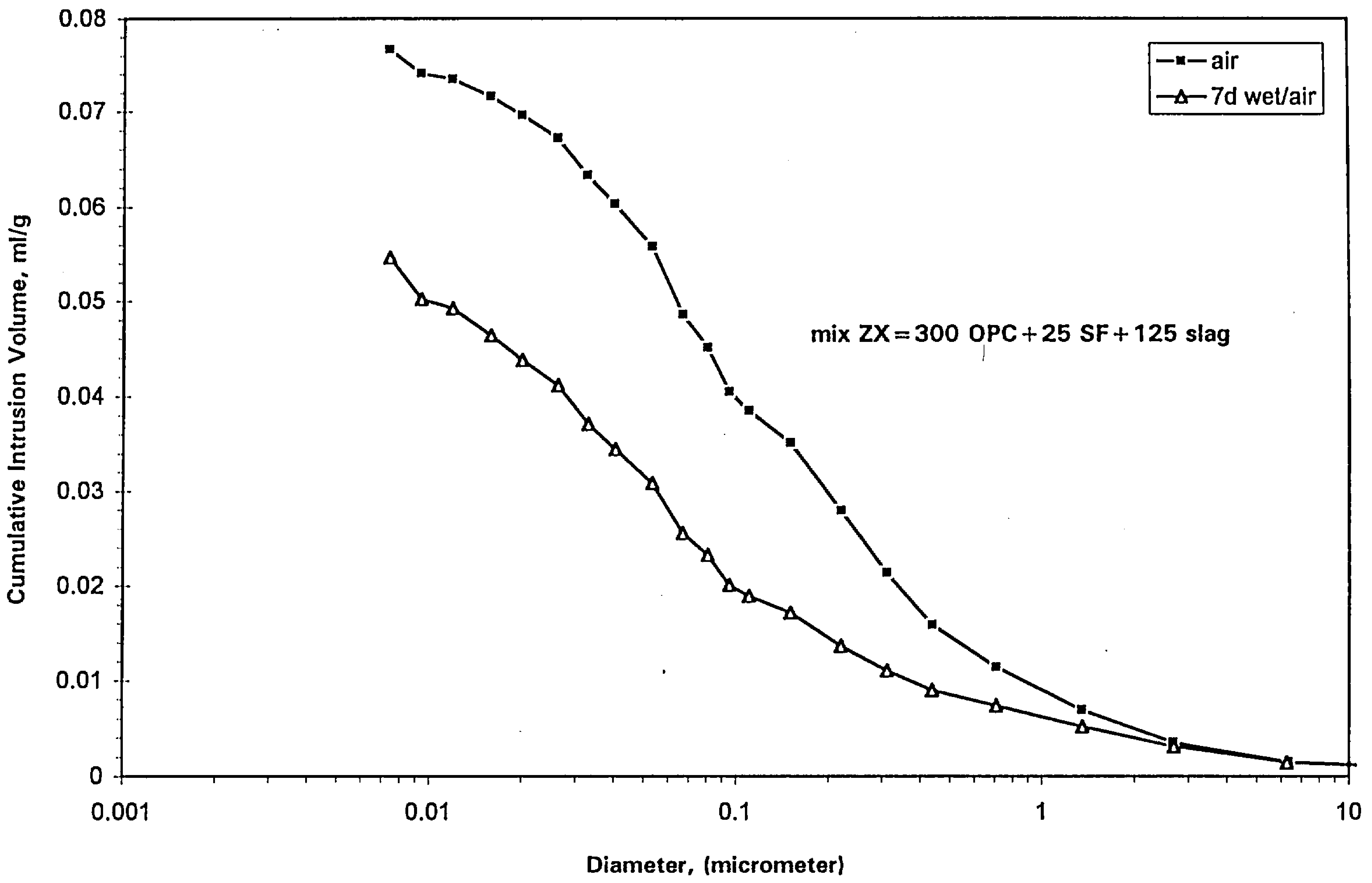


Figure 5.24 Pore size distribution at various curing condintions for mix ZX

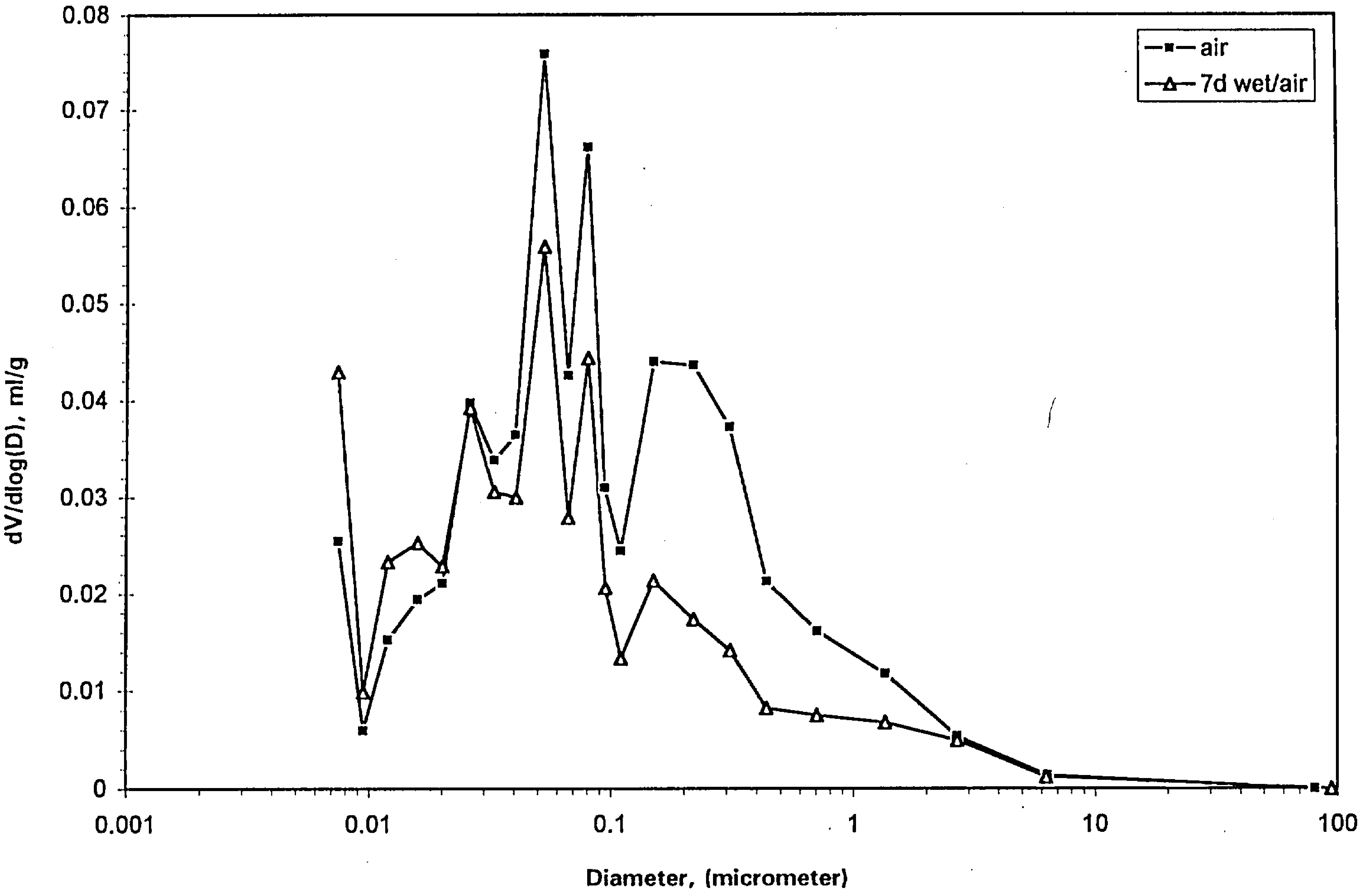


Figure 5.25 Differential pore size distribution at various curing conditions for mix ZX

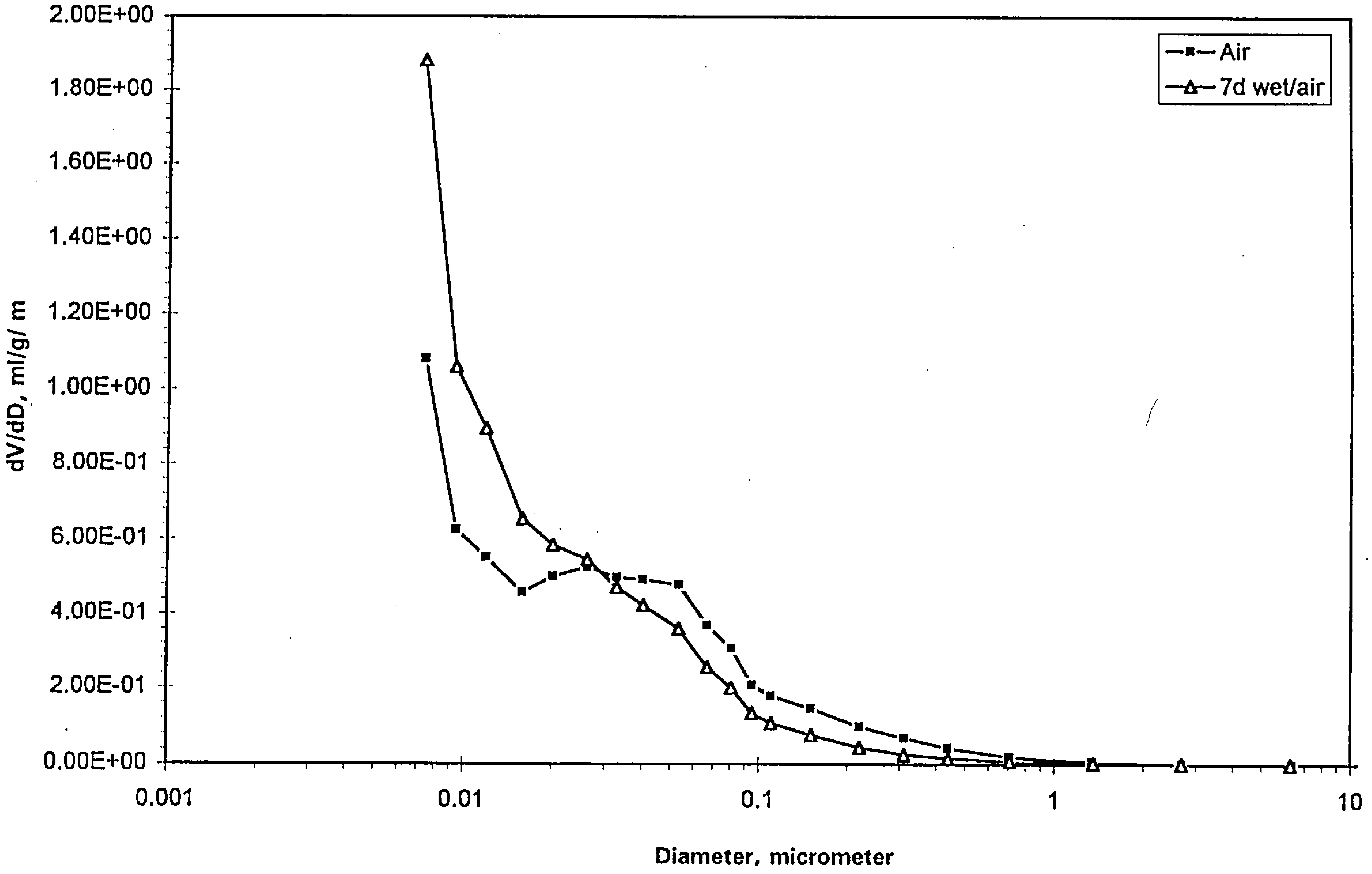


Figure 5.26 dV/dD vs. D curves at various curing conditions for mix ZX

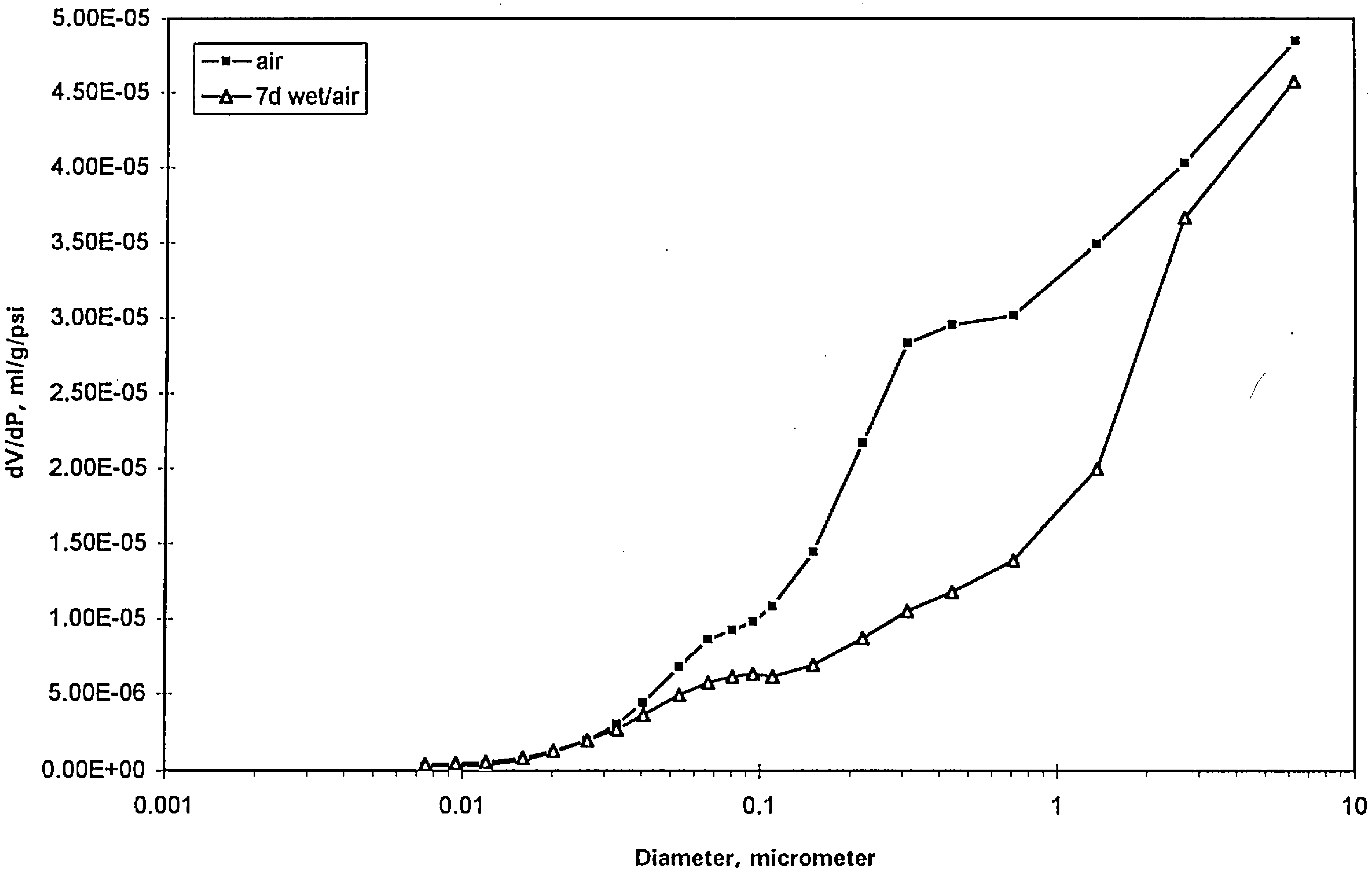


Figure 5.27 Variation of dV/dP with pore diameter for mix ZX

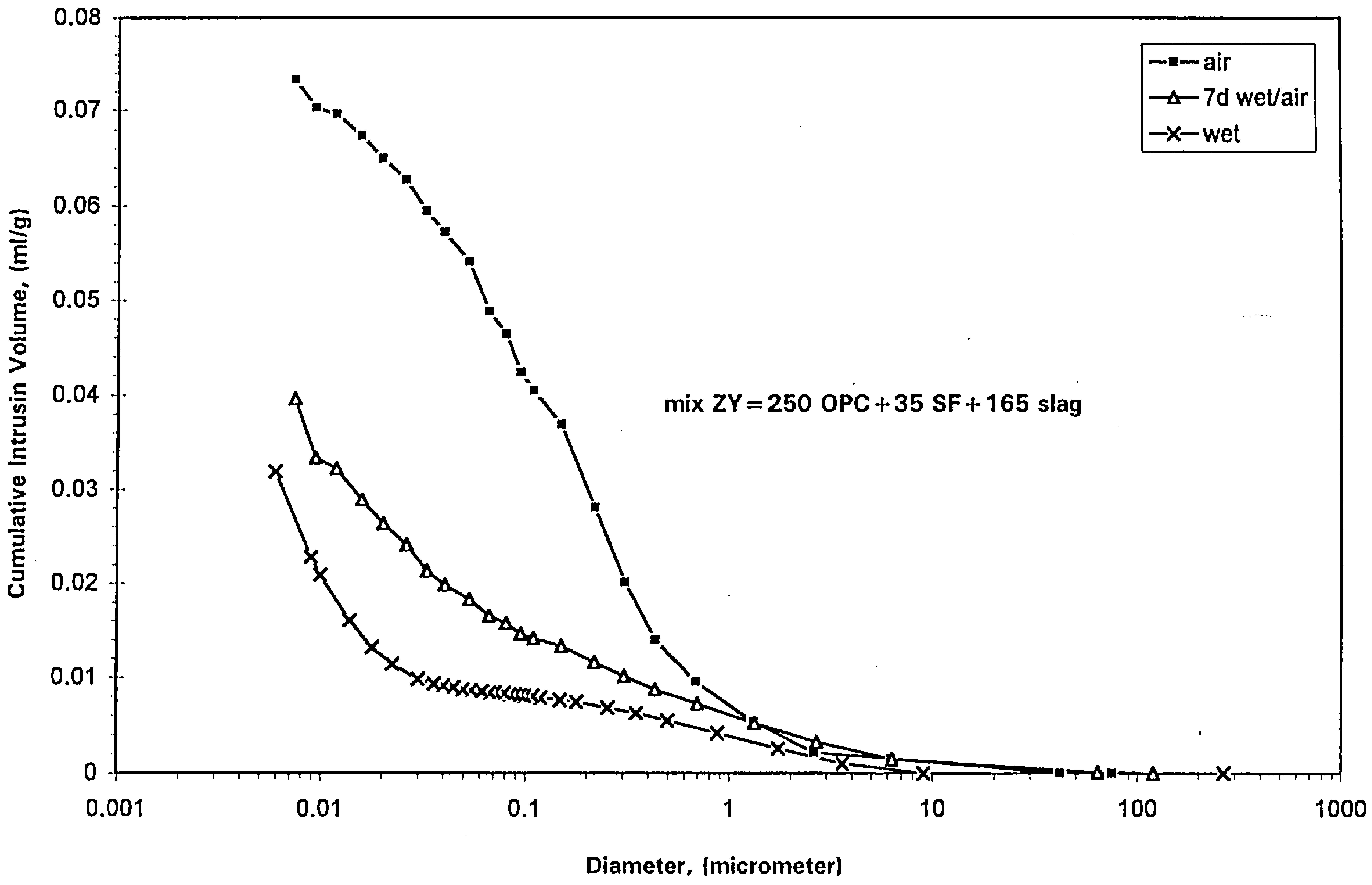


Figure 5.28 Pore size distribution at various curing conditions for mix ZY

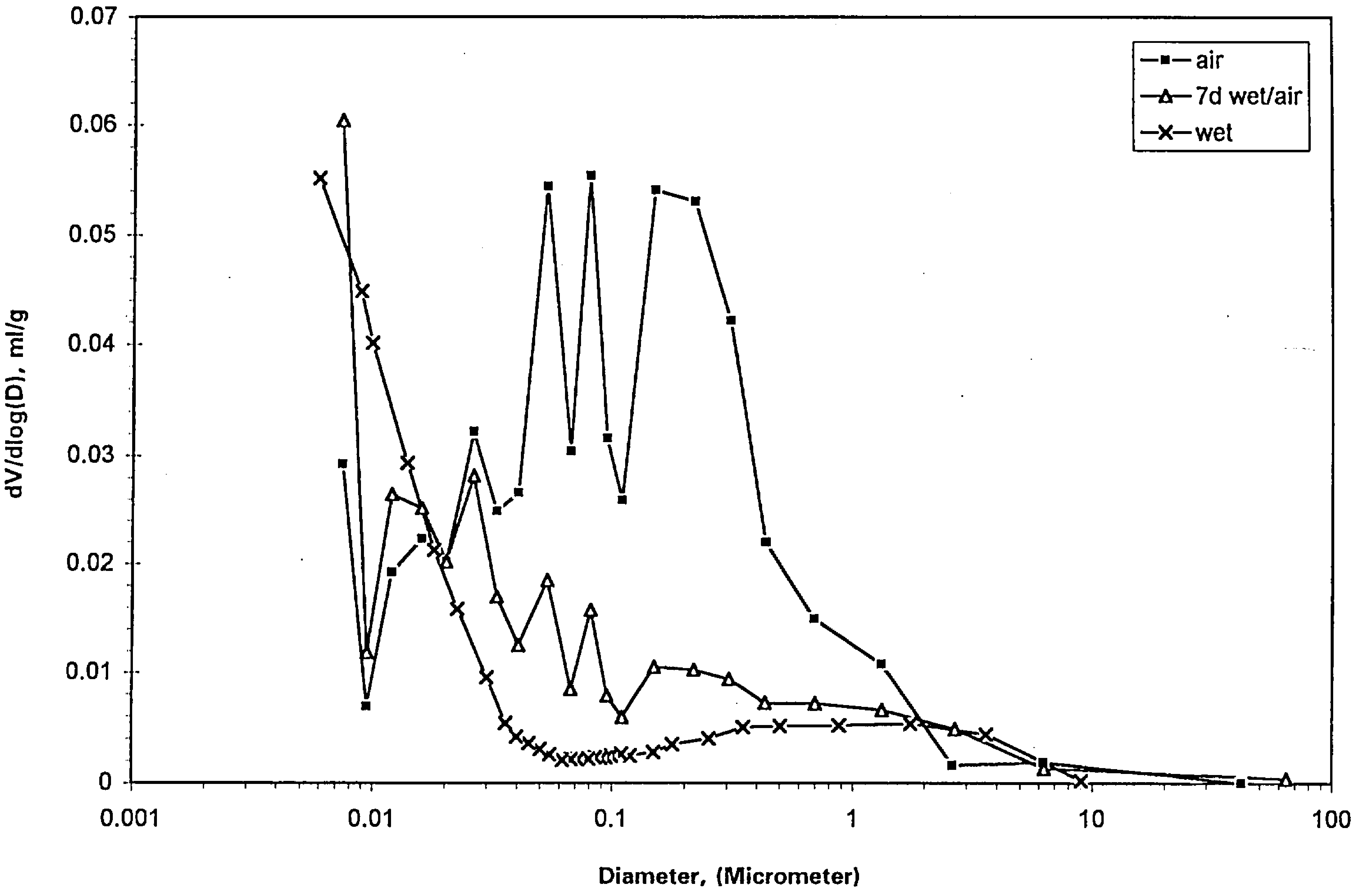


Figure 5.29 Differential pore size distribution at various curing conditions for mix ZY

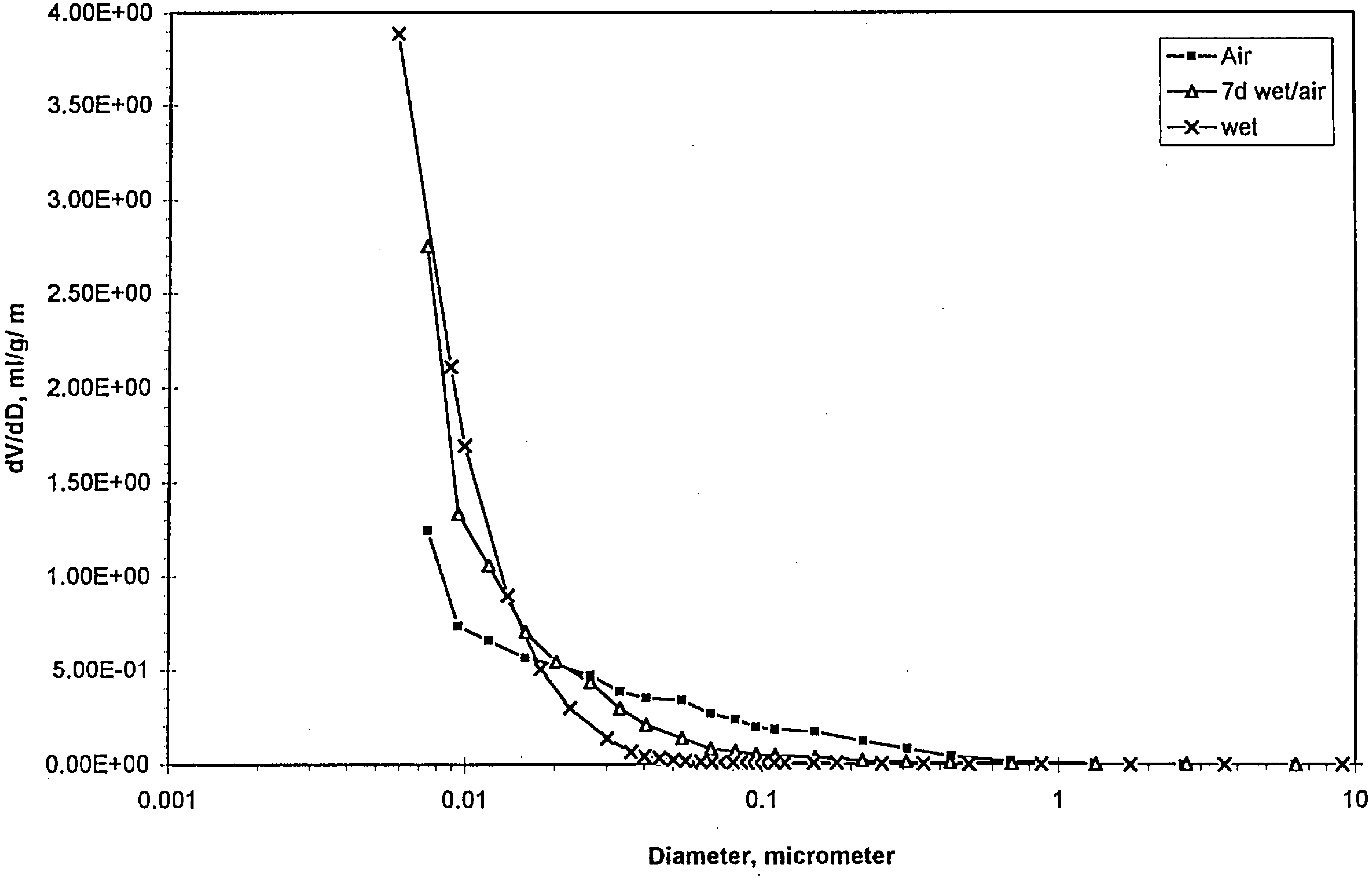


Figure 5.30 dV/dD vs. D curves at various curing conditions for mix ZY

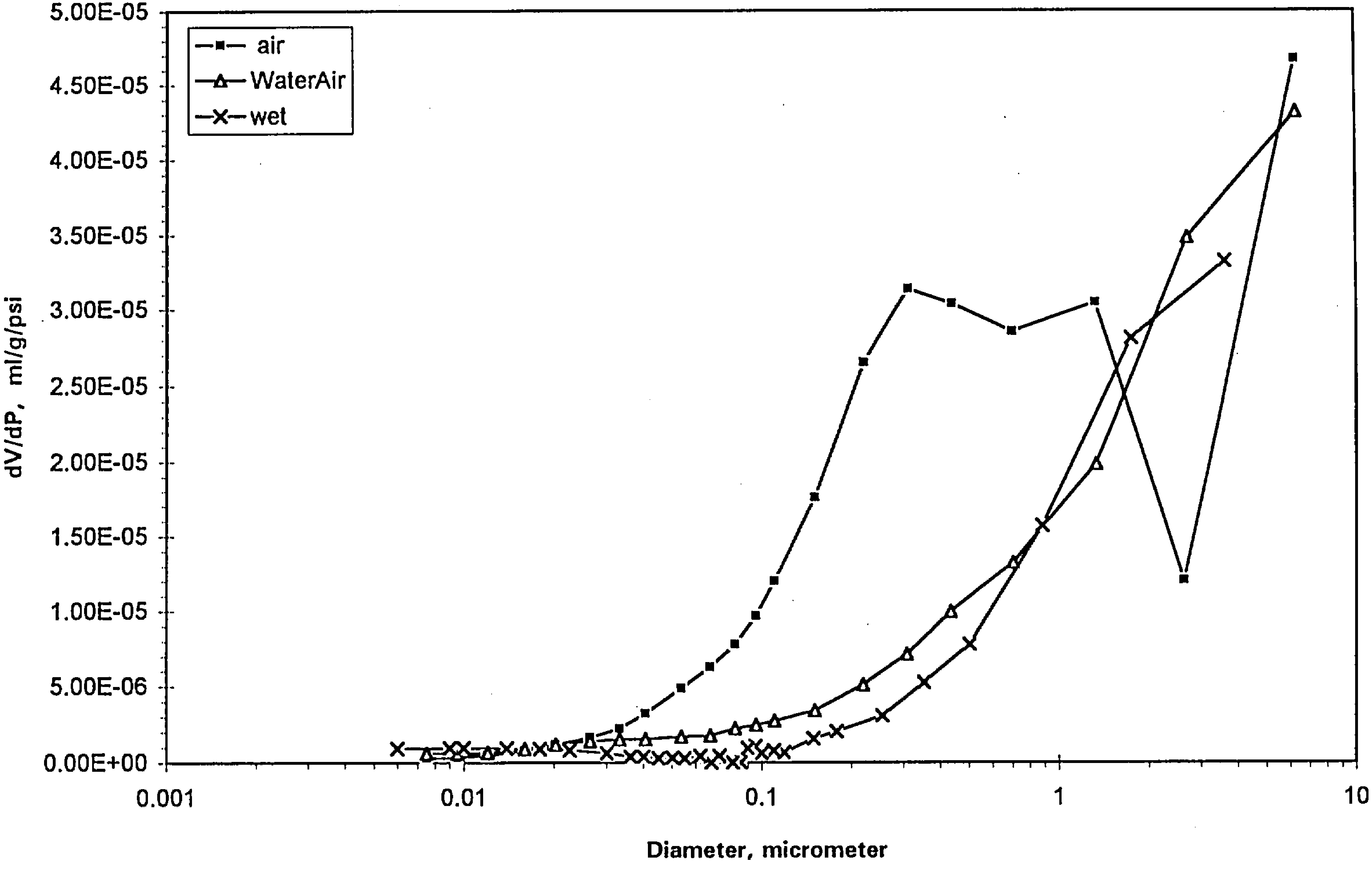


Figure 5.31 Variation of dV/dP with pore diameter for mix ZY

correlated to strength and permeability of concrete. In this work, the effect of SF, FA and slag as the replacement materials of cement on pore structure was investigated.

5.5.1 Influence of FA/SF

As mentioned earlier mix W is the control mix and mix X and mix Y are the mixes with 20kg/m^3 SF plus 30kg/m^3 FA and 20kg/m^3 SF plus 80kg/m^3 FA as the replacement materials of cement, respectively.

The results on intruded pore volume indicate that a higher pore volume was obtained in mix X and mix Y compared with mix W. This is clearly shown in Figure 5.32, where the intruded pore volumes for all mixes are presented under different curing conditions; under air-curing condition, mix X exhibited an intrusion pore volume of 0.0672 ml/g, the corresponding value is 0.0732 ml/g for mix Y which show the increases in the intruded pore volume of 26.7% and 38.1% compared with the intruded volume of 0.0530ml/g for mix W. Compared to the mix X, mix Y specimens have a larger intruded pore volume. This result shows that the intruded pore volume increases with increasing volumes of FA.

The above mentioned trend is repeated under the continuous water-curing and 7d wet/air-curing conditions. As seen from Table 5.5 and Figure 5.32, by considering the 7d wet/air-curing condition, mix X and mix Y have the intruded volume of 0.0545 ml/g and 0.0581ml/g respectively, the corresponding value is 0.0488ml/g for the control mix W. These results exhibited the increases in intruded pore volumes of 11.6% and 18.9% for mix X and mix Y respectively. For continuous water-curing condition, mix X and mix Y show similar increases in the intruded pore volume of 21.9% and 37.8% respectively. The results obtained are in good agreement with the results of Manmahan and Mehta [72], where the intruded pore volume of a mix with 30% replacement level of FA was larger than that of the control mix. This also agrees with the results obtained by Mangat and El-Khatib [23], where a 22% FA blended mix was found to possess a higher intruded pore volume than the control mix.

The results on pore size distribution under different curing conditions for mix W, mix X and mix Y are shown in Figures 5.34 to 5.45. The Figures show, generally, the tendency of coarser pores in mix X and mix Y, compared with mix W. The volume of larger pores in various mixes is presented in Figure 5.33. For air cured specimens, the volume of large pores in mix W, mix X and mix Y are 0.0160 ml/g , 0.0322 ml/g and 0.0425 ml/g respectively, the corresponding portion in total pore volume are 30.19%,

Table 5.5 Influence of cement replacement materials on porosity and on volume of large and small pores

Curing	Age of curing	Mix	Binder content, kg/m^3		Porosity	Introded pore Volume (ml/g)			Pores (%)	
	days		OPC/SF/FA	OPC/ SF/ Slag	(%)	Total pore volume	Large pores > 0.1μm	Small pores <0.1μm	Large	Small
Wet	240	W	350/0/0	350/0/0	8.67	0.0392	0.0074	0.0318	18.88	81.12
Wet	240	X	300/20/30		9.90	0.0478	0.0099	0.0379	20.71	79.29
Wet	240	Y	250/20/80		11.04	0.0540	0.0087	0.0453	16.11	83.89
Wet	240	Z		250/20/80	7.75	0.0372	0.0087	0.0285	23.39	76.61
Wet	120	ZY		300/25/165	4.95	0.0319	0.0080	0.0239	25.08	74.92
7d wet/air	240	W	350/0/0	350/0/0	11.21	0.0488	0.0164	0.0324	33.60	66.39
7d wet/air	240	X	300/20/30		11.30	0.0545	0.0167	0.0378	30.64	69.39
7d wet/air	240	Y	250/20/80		11.72	0.0581	0.0186	0.0395	32.01	67.99
7d wet/air	240	Z		250/20/80	9.00	0.0433	0.0126	0.0307	29.10	70.90
7d wet/air	240	ZX		300/25/125	10.76	0.0546	0.0189	0.0357	34.62	65.38
7d wet/air	120	ZY		250/35/165	8.07	0.0396	0.0141	0.0255	35.61	64.39
Air	240	W	350/0/0	350/0/0	11.42	0.0530	0.0160	0.0370	30.19	69.81
Air	240	X	300/20/30		14.16	0.0672	0.0322	0.0350	47.92	52.08
Air	240	Y	250/20/80		15.17	0.0732	0.0425	0.0307	58.06	41.94
Air	240	Z		250/20/80	14.61	0.0702	0.0399	0.0303	56.84	43.16
Air	240	ZX		300/25/125	15.10	0.0767	0.0384	0.0383	50.06	49.94
Air	120	ZY		250/35/165	14.34	0.0733	0.0404	0.0329	55.12	44.88

47.92%, 58.06%, respectively. This result has shown that concretes containing FA have a higher volume of large pores than of the control mix, and with an increased volume of FA replacement, the greater the volume of large pores.

As seen from Figure 5.33, under 7d wet/air-curing and water-curing, the proportion of large pores for mixes X and Y is much smaller than the corresponding value under air-curing. These values are 33.60%, 30.64%, 32.01% for mixes W, X and Y respectively. This result showed that concretes containing FA have almost the same volume of large pores as the control mix due to greater hydration of both cement and FA. A comparison of 7d wet/air-curing and air-curing specimens shows that the FA blended mixes are more susceptible to dry curing than the OPC mixes. This shows that the lack of moisture for hydration, under air-curing, has a more critical effect on FA blended mixes, and increases when a higher replacement amount is used.

Under the continuous water-curing conditions, the proportion of large pores for mix W, X and Y is smaller than the corresponding values under 7d wet/air-curing conditions. As seen from Table 5.5 the fractions of large pores in total pore value are 18.88%, 20.71% and 16.11% respectively. It should be noted that mix Y containing 80kg/m^3 FA has the lowest proportion of large pores in all mixes. This shows that the moisture for hydration has a more critical effect on FA blended with concrete than on the OPC concrete.

Shigun Li and Roy [121] reported increased intruded pore volume in a 20% FA blended mix compared with the control mix. Specimens were cured for 28 days at 38°C in saturated deionised water and the water/binder ratio varied from 0.3 to 0.6. The increase in the intruded pore volume in their study varied from 5 to 23.8%, yet the blended FA paste indicated finer pore structure compared with the control paste. This also happens in this investigation. Table 5.5 shows a higher total pore volume for mix X and mix Y compared with mix W. In this study, the increase in the intruded pore volume varied from 11.6% to 38.1%, depending on the curing conditions and the FA replacement amount. However, a finer pore structure was not found compared to the control mix

Figures 5.34 to 5.37 have shown the effects of FA on pore size distribution under air-curing condition. As seen from Figure 5.34 threshold diameter of mix W is 0.27 μm, and it is 0.5μm and 0.7μm for mix X and mix Y, respectively. Similar results can also be observed from dv/dlog D-D, dv/dD-D and dv/dp-D curves in Figures 5.35-5.37. This fact clearly shows that the addition of FA induces a larger threshold diameter of concrete under air-curing condition. The larger the amount of FA, the higher is the threshold diameter.

Under 7d wet/air-curing condition, mix W, mix X and mix Y exhibited almost the same threshold diameter, as shown in Figure 5.38. This result shows that water-curing at an early stage is especially important for the concrete containing FA. Figures 5.42 - 5.45 presents the effect of FA on pore structure distribution under water-curing condition, whereas the opposite situation of concrete cured in air, showed that the concrete containing the FA exhibited a smaller threshold diameter than concrete without FA. As shown in Figure 5.42 the threshold diameter is 0.08μm for concrete mix W, and corresponding value is 0.055μm for both mix X and mix Y.

From the above mentioned results, the following conclusions can be drawn:

1. The addition of FA increases the intruded pore volume of specimens under the three kinds of curing conditions. The intruded pore volume increases with increased amount of FA.

2. The finer pore structure was not observed in the concrete containing FA. Under both 7d wet/air-curing and water-curing conditions, the large pore ($D > 0.1\mu m$) volume of concretes containing FA was a little larger than that of the control mix specimen. Under air-curing conditions, their large pore volume was much greater than the control mix concrete.

3. Concretes containing FA have a smaller threshold diameter than control mix under water-curing conditions. Under 7d wet/air-curing conditions, their threshold diameters are the same as that of control mix. However under air-curing, their threshold diameters are much larger than control mix. It could be concluded that only when under sufficient water-curing the addition of FA can improve the pore structure.

5.5.2 Influence of Slag/SF

The effect of SF and slag was investigated in this work. Mix Z was made with 20 kg/m^3 SF and 80kg/m^3 slag as the replacement materials of cement. Mix ZX and mix ZY had different mix proportions: mix ZX contained 300kg/m^3 cement, 25kg/m^3 SF and 125kg/m^3 slag while mix ZY contained 250kg/m^3 cement, 35kg/m^3 SF and 165kg/m^3 slag. Mix W with the 350kg/m^3 cement content was the control mix.

The result has shown that mix Z with SF and slag as replacement materials of cement has a smaller or larger intruded pore volume compared with mix W as shown in Table 5.5 and Figure 5.32. Mix Z has larger intruded pore volume under air-curing compared with mix W, which is 0.0702ml/g, an increase of 32.5% compared to mix W. However, under both continous water-curing and 7d wet/air-curing mix Z exhibited a smaller amount of intruded pore volume compared with mix W. For example, under 7d wet/air-curing, mix Z exhibited an intruded pore volume of 0.0433 ml/g which is a decrease in intruded pore volume of 11.3% compared with the intruded volume of 0.0488 ml/g for mix W. The above mentioned results show that the 80kg/m^3 slag blended mixes is more susceptible to dry-curing than the OPC and 30kg/m^3 FA blends. This is clear in Table 5.5 and Figure 5.32 where the control mix W shows almost a similar introduced pore volume, between 7d wet/air-cured specimens and air cured specimens, whereas an increase of 23.3% and 62% was obtained for 30kg/m^3 FA blends and 80kg/m^3 slag blends mixes respectively. This shows that the lack of moisture for hydration, under air-curing, has a more critical effect on slag blends and FA blends, and the effect is much greater with a slag blend mix compared with other replacement materials.

Similar results were also obtained by Mangat and El-Khatib research [23] where 40% slag blended paste exhibited a larger intruded pore volume, compared with air-curing OPC mix under air-curing condition. The water/cement ratio was 0.45 and the age of curing was six months.

The results on pore size distribution under different curing conditions for mix W, mix Z, mix ZX and ZY are shown in Figures 5.46-5.57. As seen from Figure 5.46 to 5.49, under air-curing, as expected, all slag concretes show significantly higher total pore volume and coarser pores compared with the control mix. The 125 and 165kg/m^3 slag concretes show the poorest performance i.e. the highest pore volume of 0.0767 and 0.0733ml/g. The volume of large pores in mix W, mix Z, mix ZX and mix ZY are 0.0160ml/g, 0.0399ml/g, 0.0384ml/g and 0.0404ml/g, respectively. This indicates that dry curing, in addition to creating a larger pore volume results in a larger pore size owing to seizure of hydration when water is not present.

Under 7d wet/air-curing conditions, i.e. subjecting the concretes to 7 days of moist curing, Figures 5.50 to 5.53, improves significantly the performance of the slag concretes, and the total pore volume values were lower than that obtained by the control mix. This curing condition does not significantly affect the performance of the control mix. Mix Z and mix ZY with slag and SF exhibited finer pore structure than control mix W, mix ZX has an almost similar pore structure compared with mix W. As seen from Table 5.5 the volume of large pores are 0.0164 ml/g,, 0.0126 ml/g, 0.0141 ml/g and 0.0189 ml/g for mix W, mix Z, mix ZY and mix ZX, respectively. Wet/air-cured specimens experienced greater hydration compared to air-cured specimens during the first 7 days of initial moist curing, resulting in a finer pore structure.

Under continuous curing conditions, Figures 5.54 to 5.57, the 165kg/m^3 slag concrete shows the lowest total pore volume. This is followed by 80kg/m^3 slag concrete, control concrete, 30 and 80kg/m^3 FA concretes, respectively. Similarly the 165kg/m^3 slag concrete yielded the finer pore structure than the other blended cement concretes. The large pore volume >1000A were 0.0080, 0.0087, 0.0087 and 0.0099ml/g for mixes ZY, Z, X and Y, respectively. The corresponding values for 7d wet/air-cured specimens were significantly higher. This indicates that high slag replacement could create fine pores under good curing and coarse pores under insufficient curing. The beneficial effects of the use of slag/SF are being reflected in the above results and an increased durability would be predicted. Swamy [19] reported, that all the benefits of slag replacements, even at high additions, can be realized if blended cement is allowed to fully hydrate and achieve its strength and durability potential.

Manmohan and Mehta [72] found that 30% slag blended paste gave 16.7% lower pore volume than the cement paste at the age of 28 days; the pastes were cured in an airtight container. In other words, water was retained in the pores.

Shigun Li and Roy [121] obtained little differences in the intruded pore volume between 65% slag blended pastes and pure cement pastes at 28 days of curing at 38°C. Specimens were cured in deionized water.

Kumar and Roy [122] showed that 65% slag blended pastes have a much lower porosity, reductions of 39% of 27°C, 54% at 38°C and 45.5% at 60°C occur at the age of 28 days for water/binder ratio of 0.35. The reductions were even greater at later ages.

Introducing slag into a cement paste has been shown to yield a finer pore structure than pure cement paste [72,121,125]. Ramezaniapour and Malhotra [43] found that 25 and 50% slag blended mortars, yielded higher total porosity and cummulative intrusion volume compared with control mortar after 28 days of moist curing. The results of this investigation are contrary to Ramezaniapour's observations. They [43] attributed their lower results to the slow rate of hydration reactions for the slag blend and that pore size distribution were performed at 28 days rather than 180 days, a more desirable age especially when supplementary cementing materials are being used. On the other hand, the 28 days compressive strength of 25% slag concrete was higher than the control and 50% slag concretes [43], similar to this study's compressive results.

The threshold diameters of concrete containing slag were larger than concrete without replacement material under air-curing. As shown in Table 5.4 and Figure 5.46, the threshold diameters were 0.7μm, 0.45 μm and 1.5μm respectively for mix Z, mix ZX and mix ZY, whereas it was 0.27μm for mix W. Under 7d wet/air-curing the concretes containing slag have almost the same threshold diameter as concrete without replacement materials of 0.1μm with the exception of mix Z which had a 0.05μm. On the other hand, continuous water curing effects favourably the threshold diameter and pore size distribution of slag and FA concretes and results in the lowest threshold for 165 slag mix, as compared with the threshold diameter values obtained for the control and other blended cement mixes. This could be due to the development of the hydration products which would have the effect of filling up large empty spaces.

The above mentioned results have clearly shown that additions of slag and SF caused pore refinement or transformation of large pores into fine pores. The pore refinement, however, only occurs in both continuous water-curing and 7d wet/air-curing conditions. Under air-curing conditions, the pores becoming coarser was observed in concretes containing slag. This clearly underscores the importance of proper curing of concrete containing slag.

Manmoham and Mehta [72] showed that additions of pozzolonic and cementitious admixtures such as rice husk ash, FA and granulated blast furnace slag to Portland cement were instrumental in causing pore refinement or transformation of large pores into fine pores. Feldman [123] using a FA and a slag as an admixture has confined the process of pore refinement. Mehta [124] considered the conversion of high density phases and large voids in a Portland cement paste system to low density products and small voids as a result of pozzolanic reaction. This mechanism is the logical explanation for the refinement in concrete containing slag. The coarser pore structure occurring in concrete containing slag under air-curing should be attributed to insufficient hydration since without sufficient progress in the pozzolanic and cementitious reactions associated with slag, the decrease in the size and number of large voids cannot be expected.

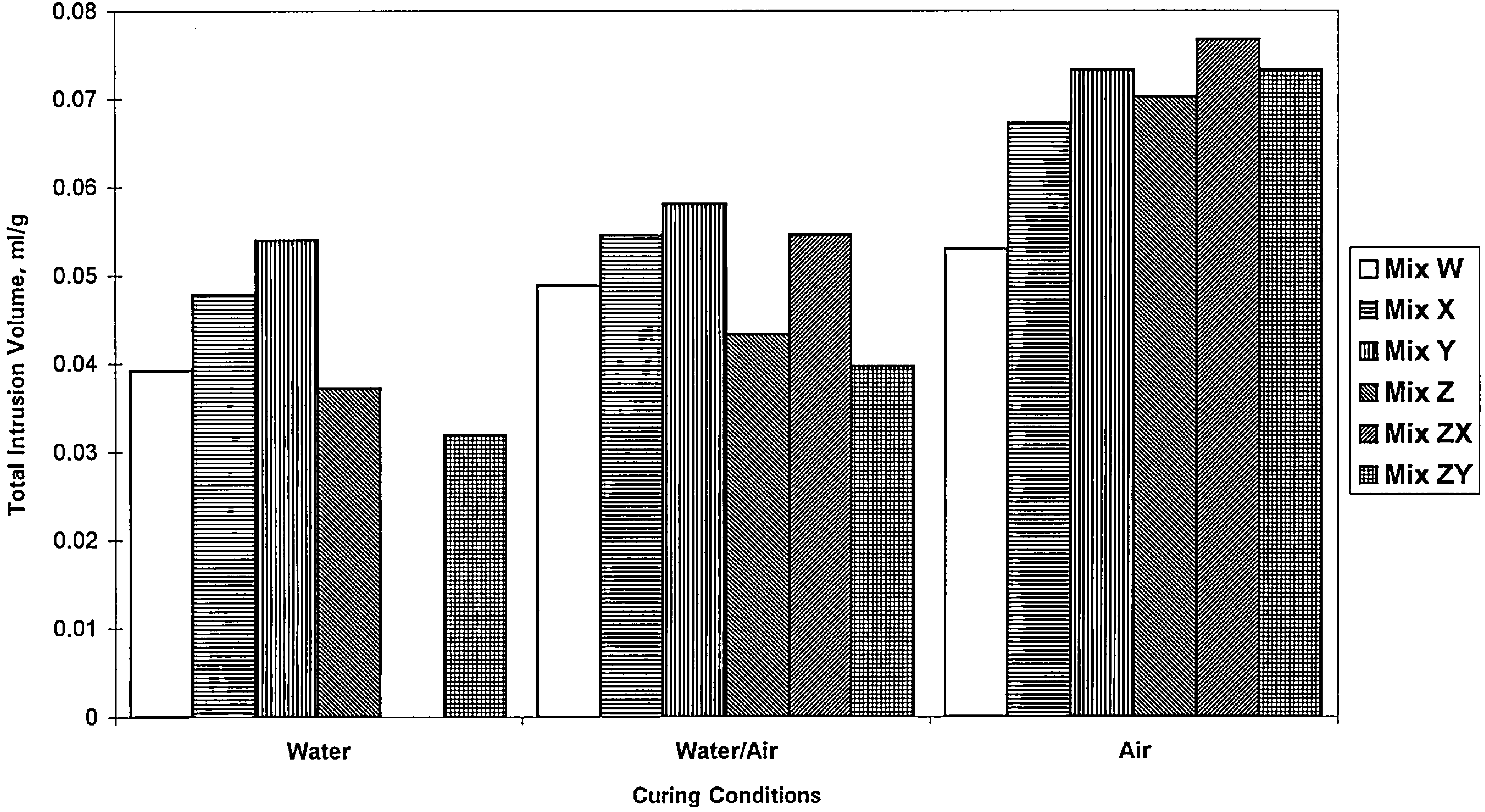


Figure 5.32 Influence of cement replacemental materials on intrusion pore volume

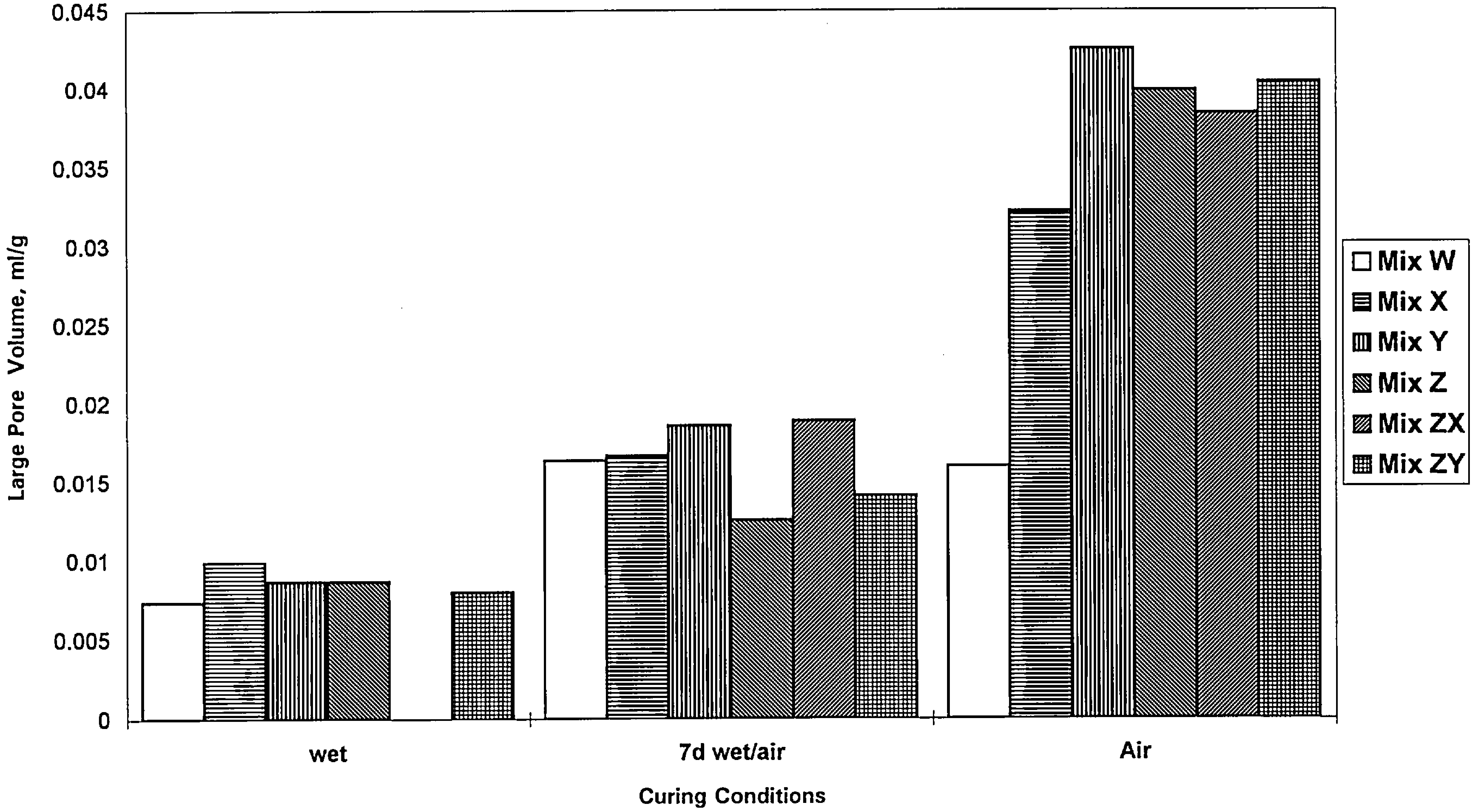


Figure 5.33 Influence of cement replacement materials on volume of large pores

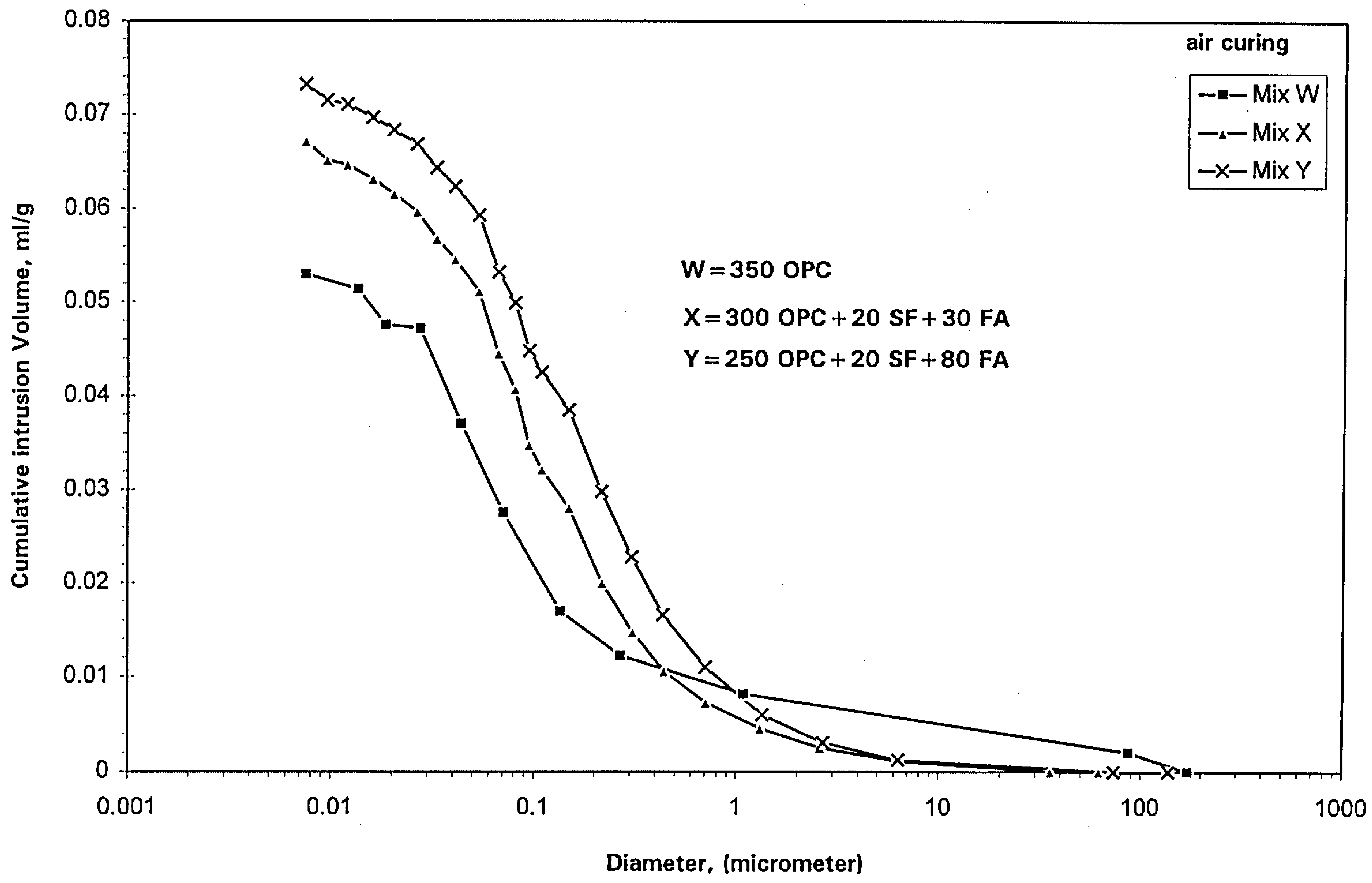


Figure 5.34 Influence of FA/SF on pore size distrubution

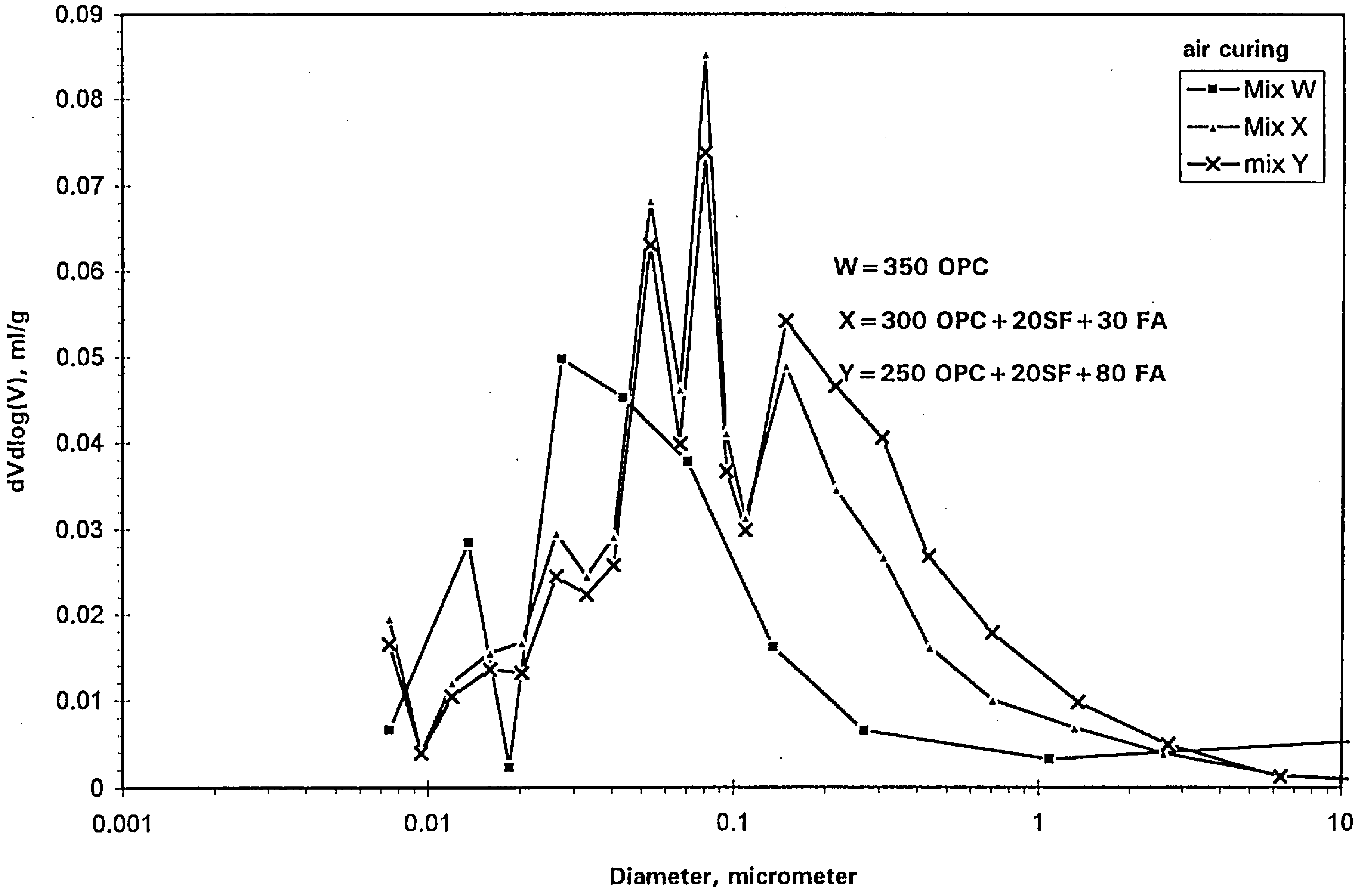


Figure 5.35 Influence of FA/SF on differential pore size distribution

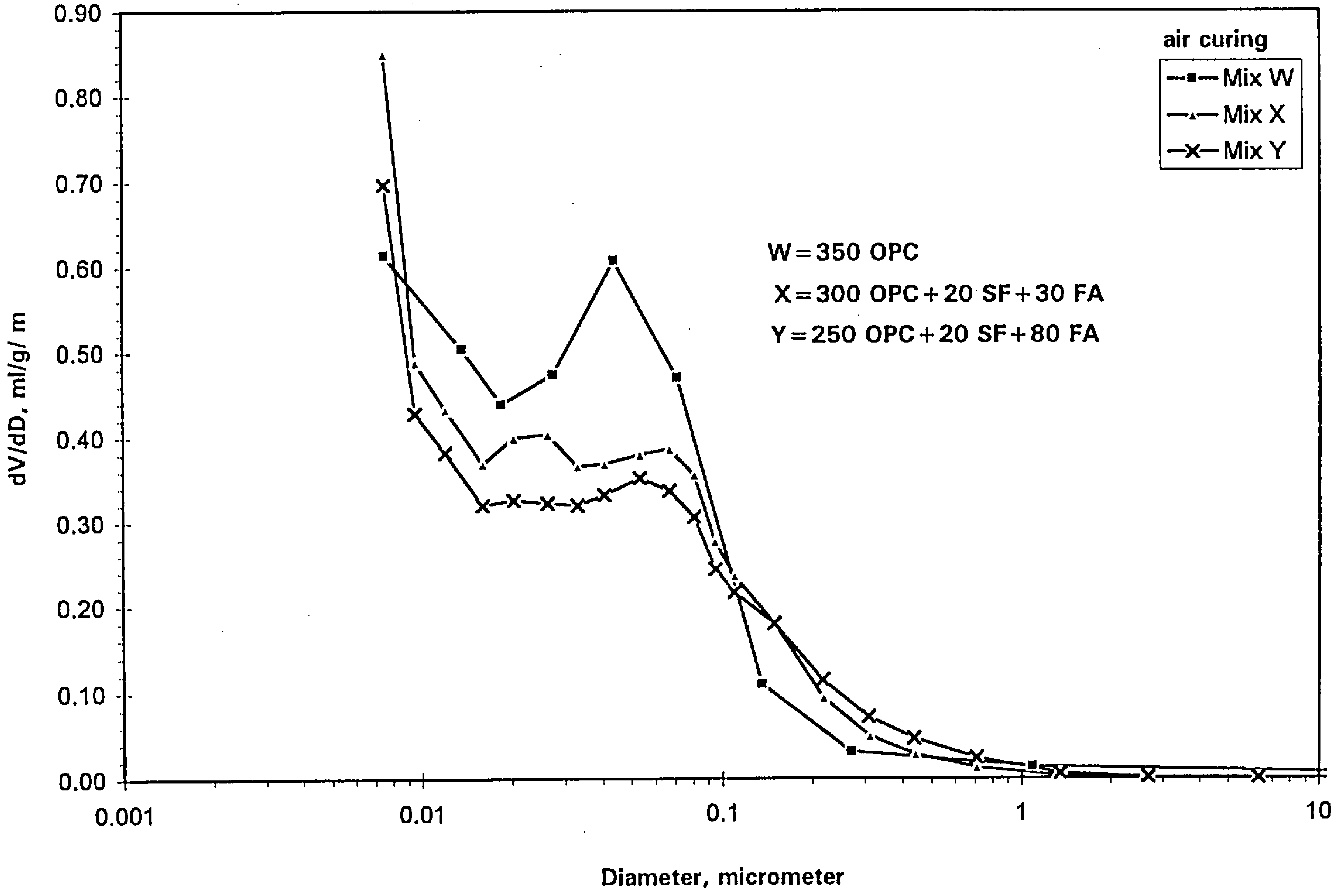


Figure 5.36 dV/dD vs. D Curves for control and FA/SF mixes

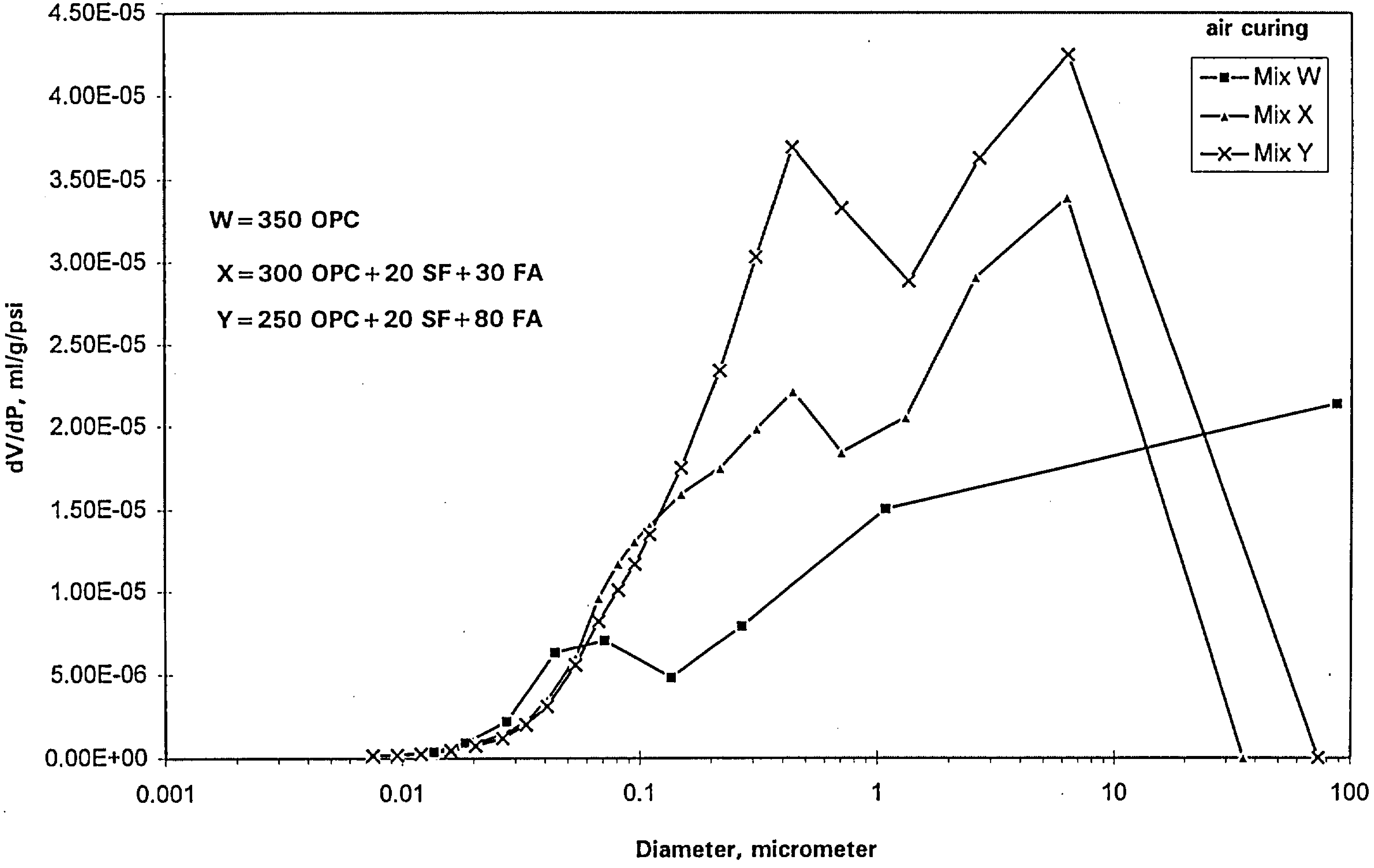


Figure 5.37 Influence of FA/SF on dV/dP variation

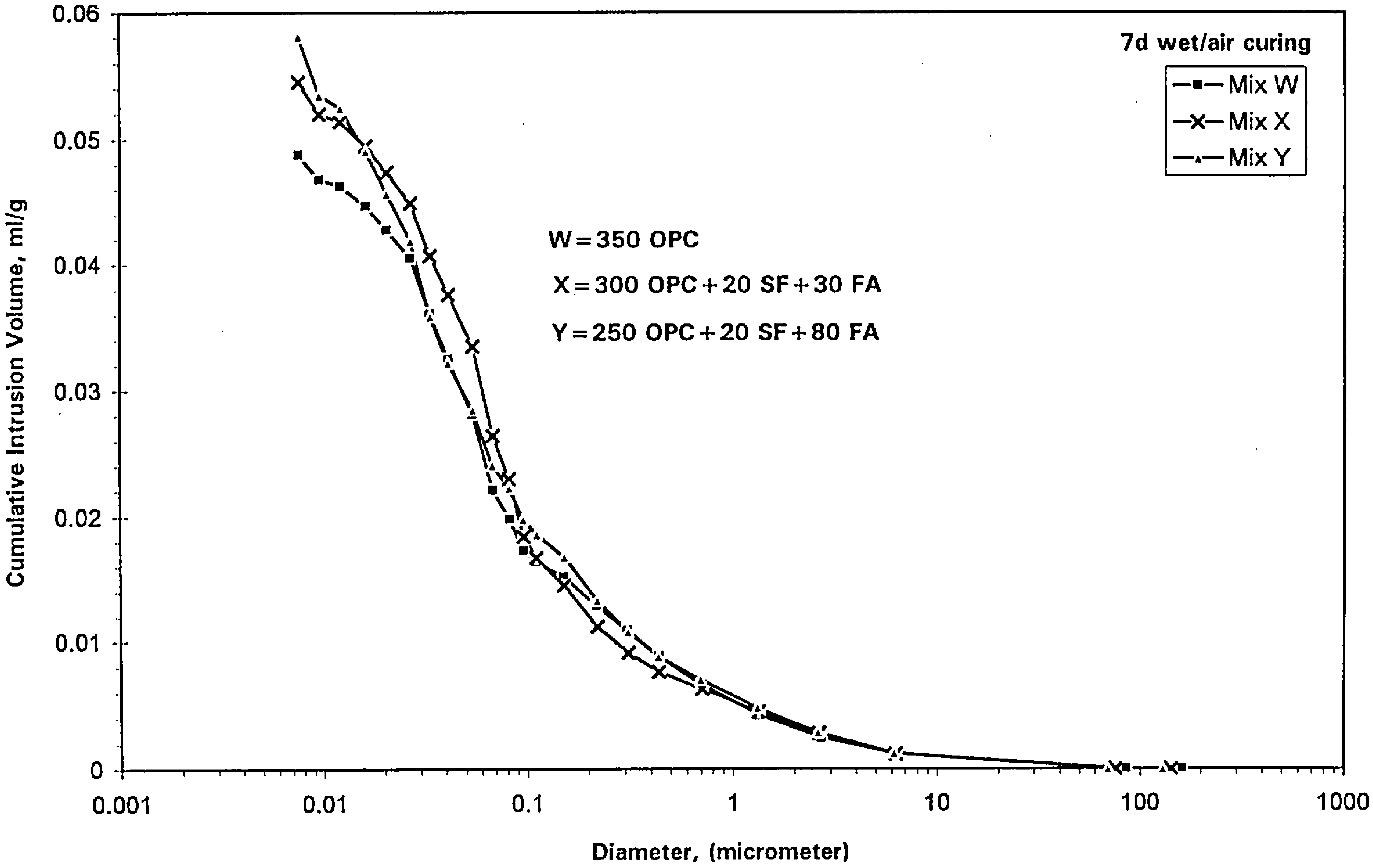


Figure 5.38 Influence of FA/SF on pore size distribution

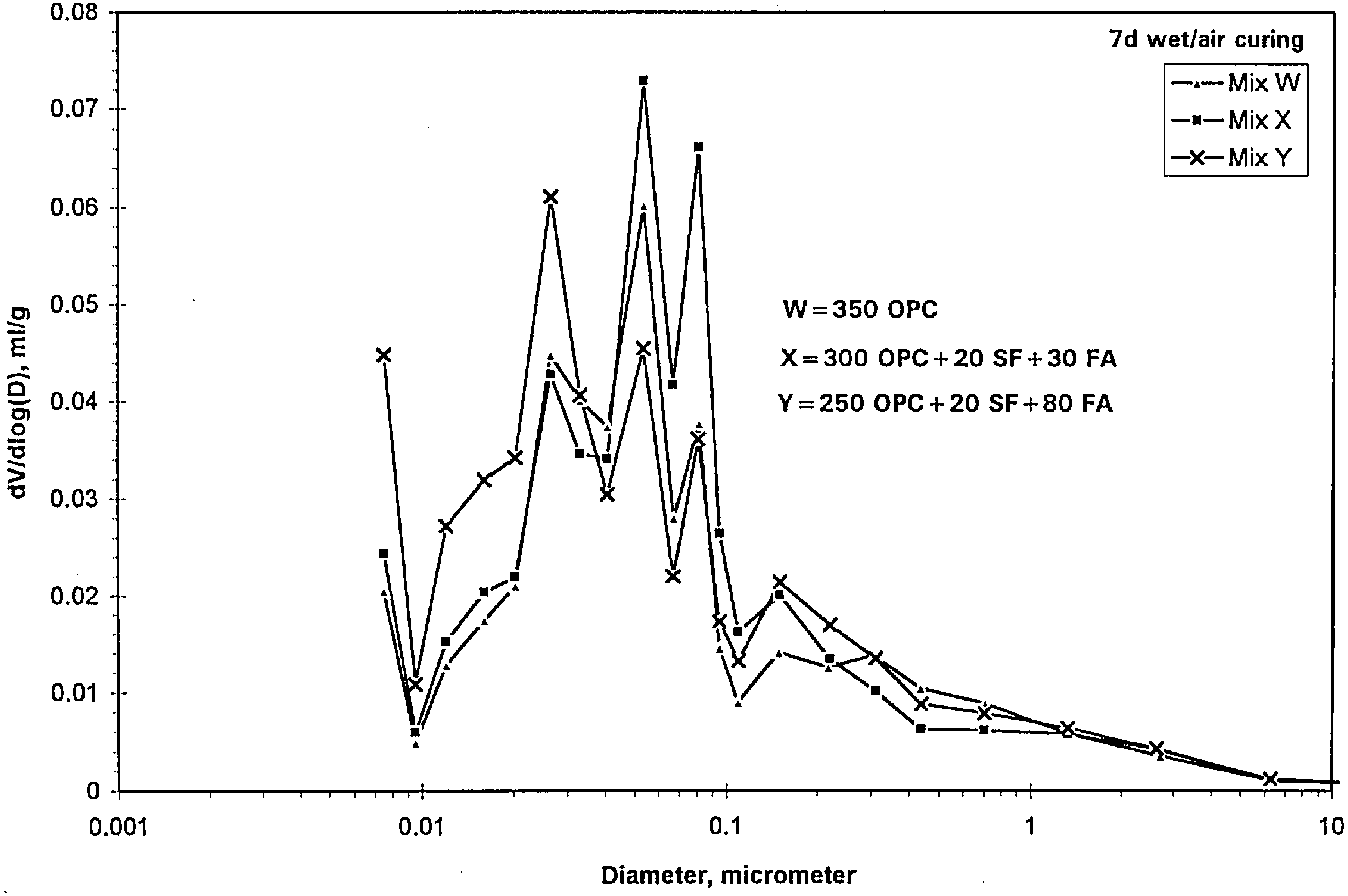


Figure 5.39 Influence of FA/SF on differential pore size distribution

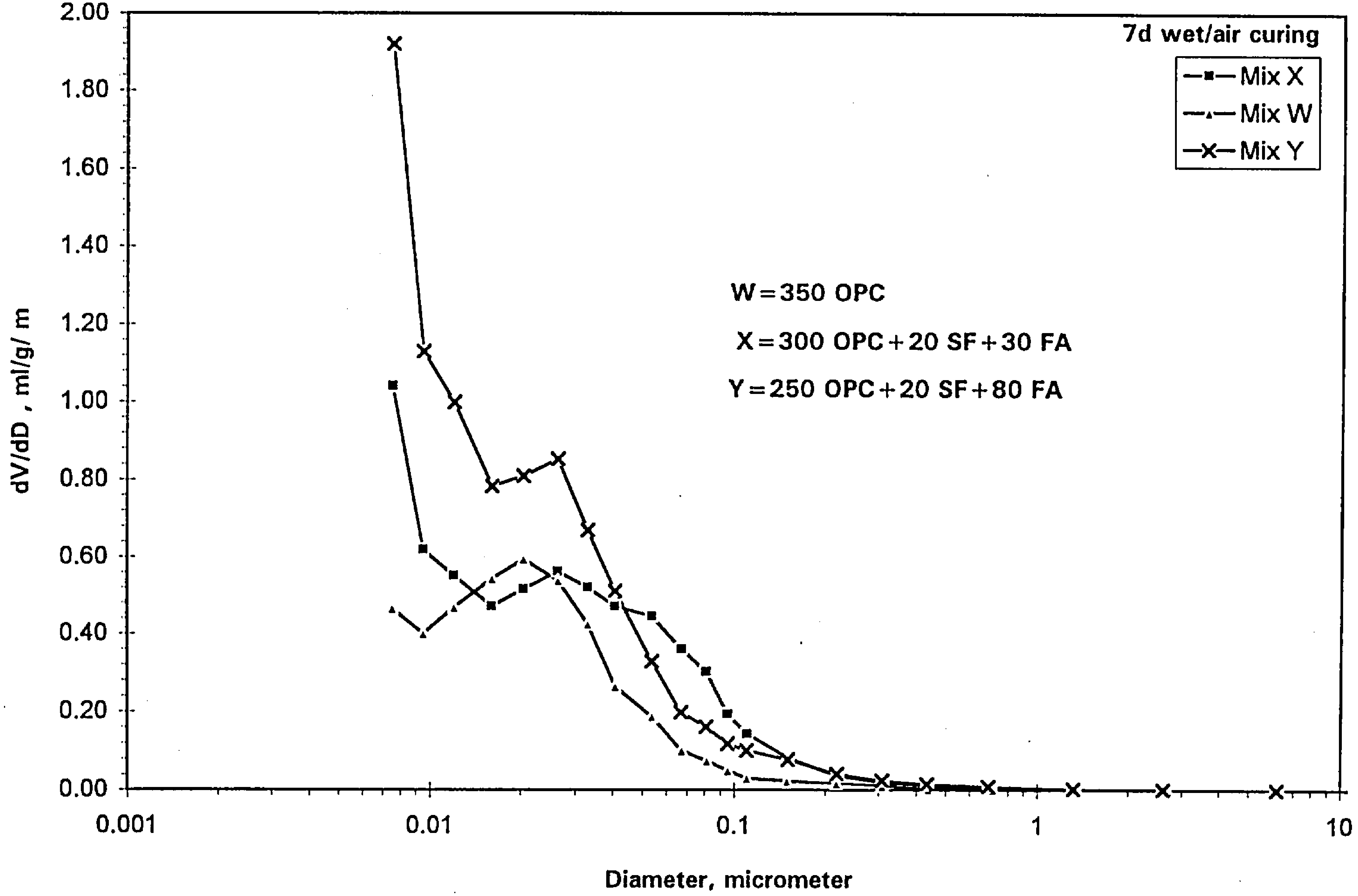


Figure 5.40 dV/dD vs. D curves for Control and FA/SF mixes

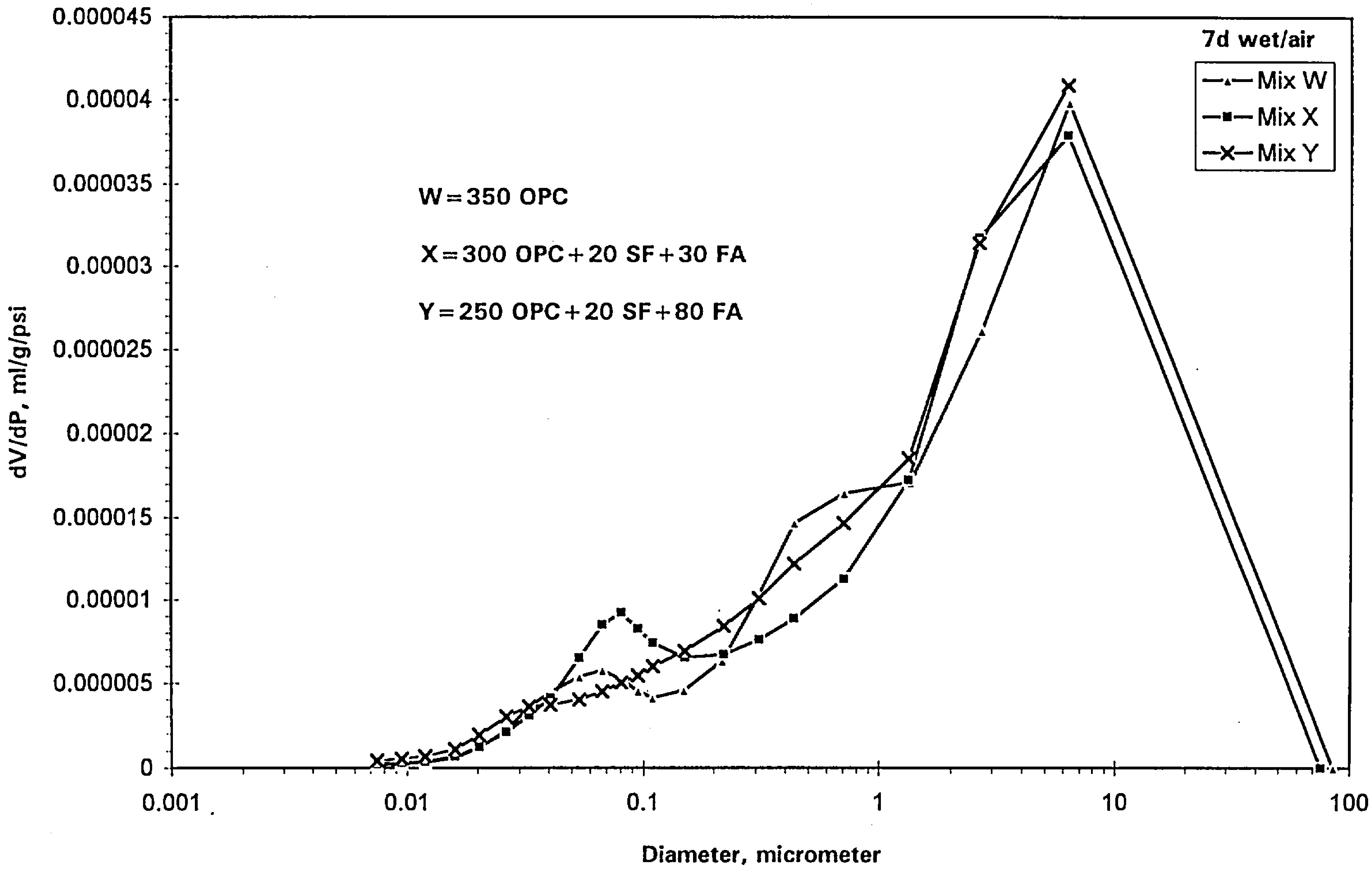


Figure 5.41 Influence of FA/SF on dV/dP variation

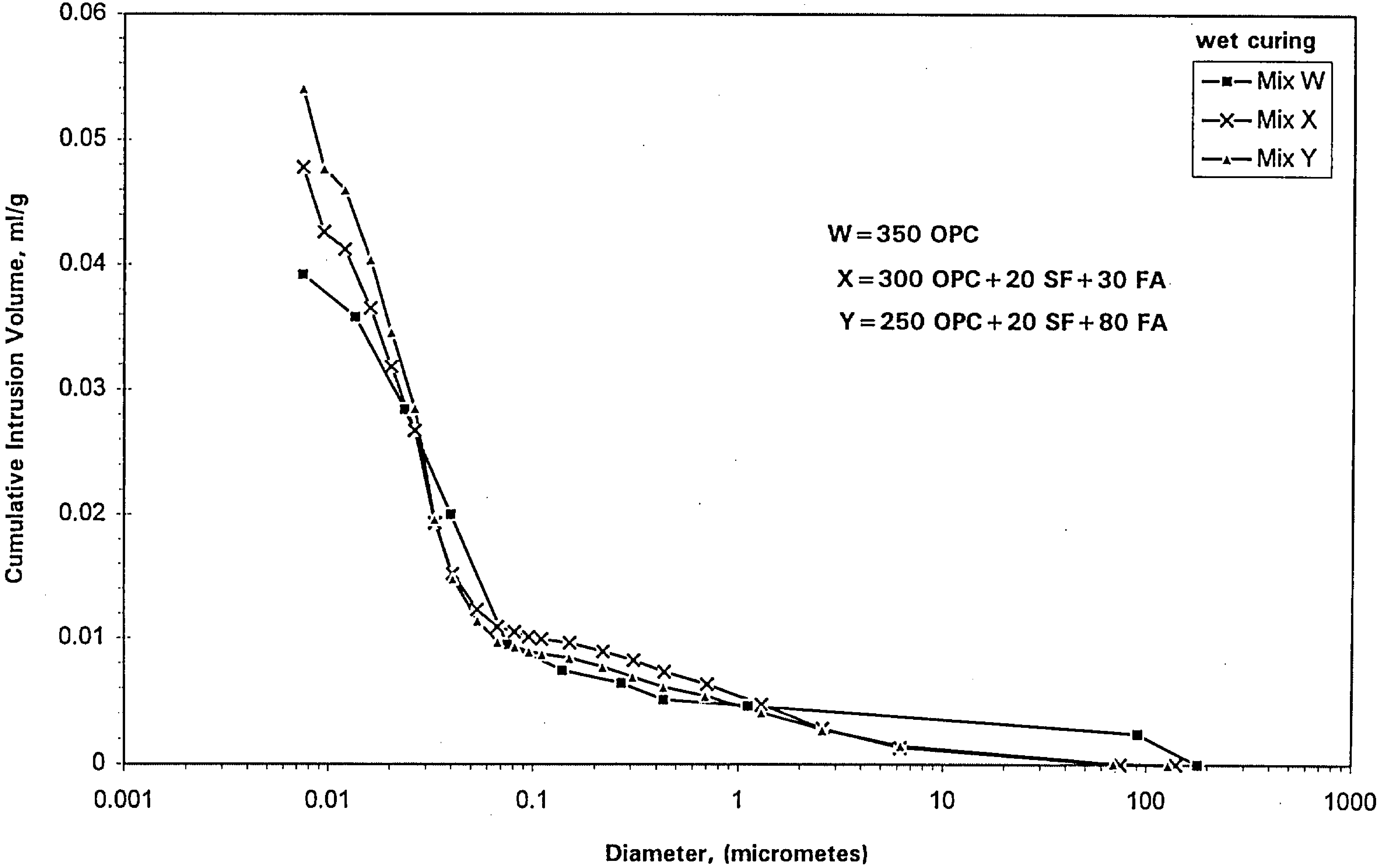


Figure 5.42 Influence of FA/SF on pore size distribution

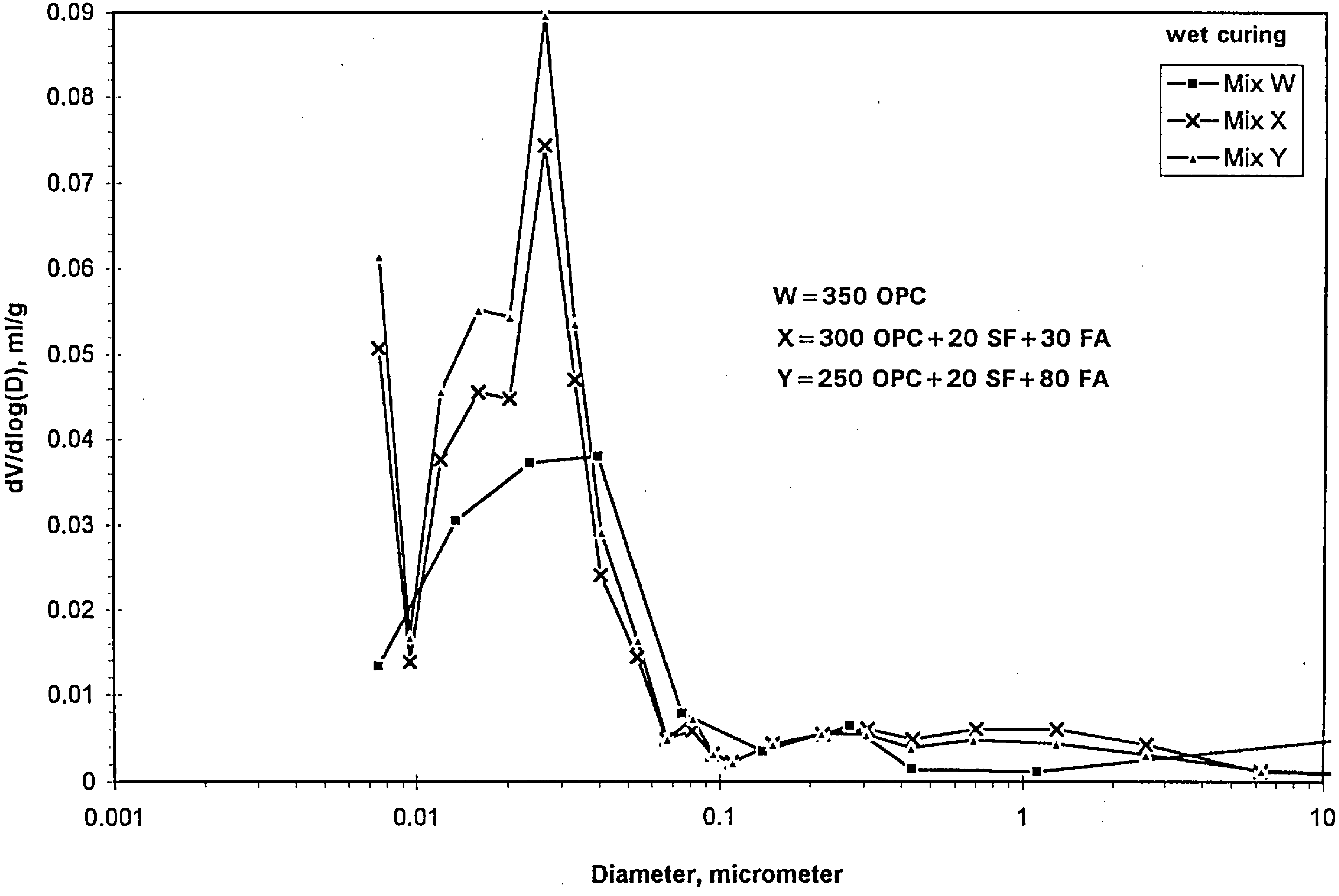


Figure 5.43 Influence of FA/SF on differential pore size distribution

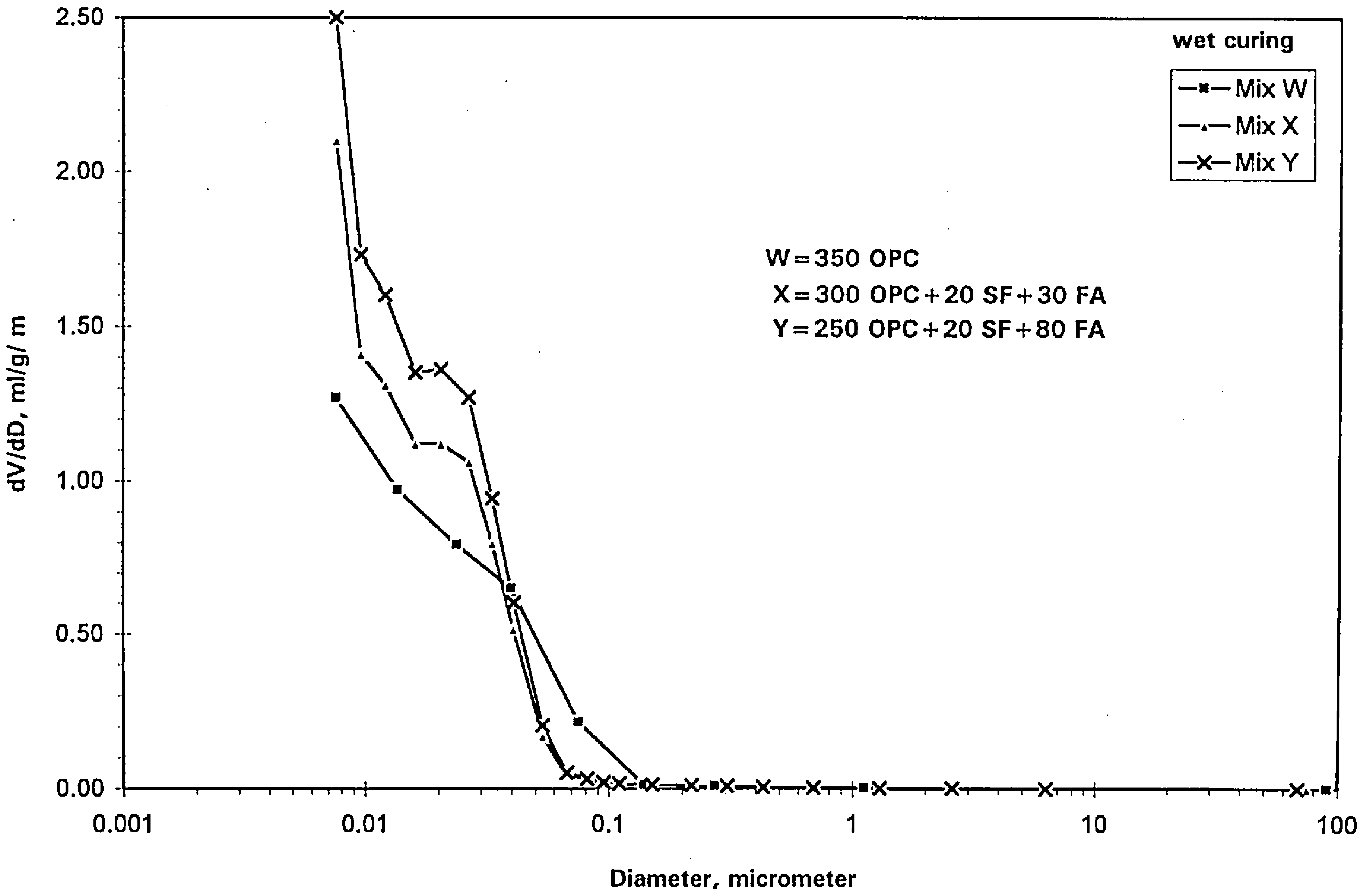


Figure 5.44 dV/dD vs. D curves for control and FA/SF mixes

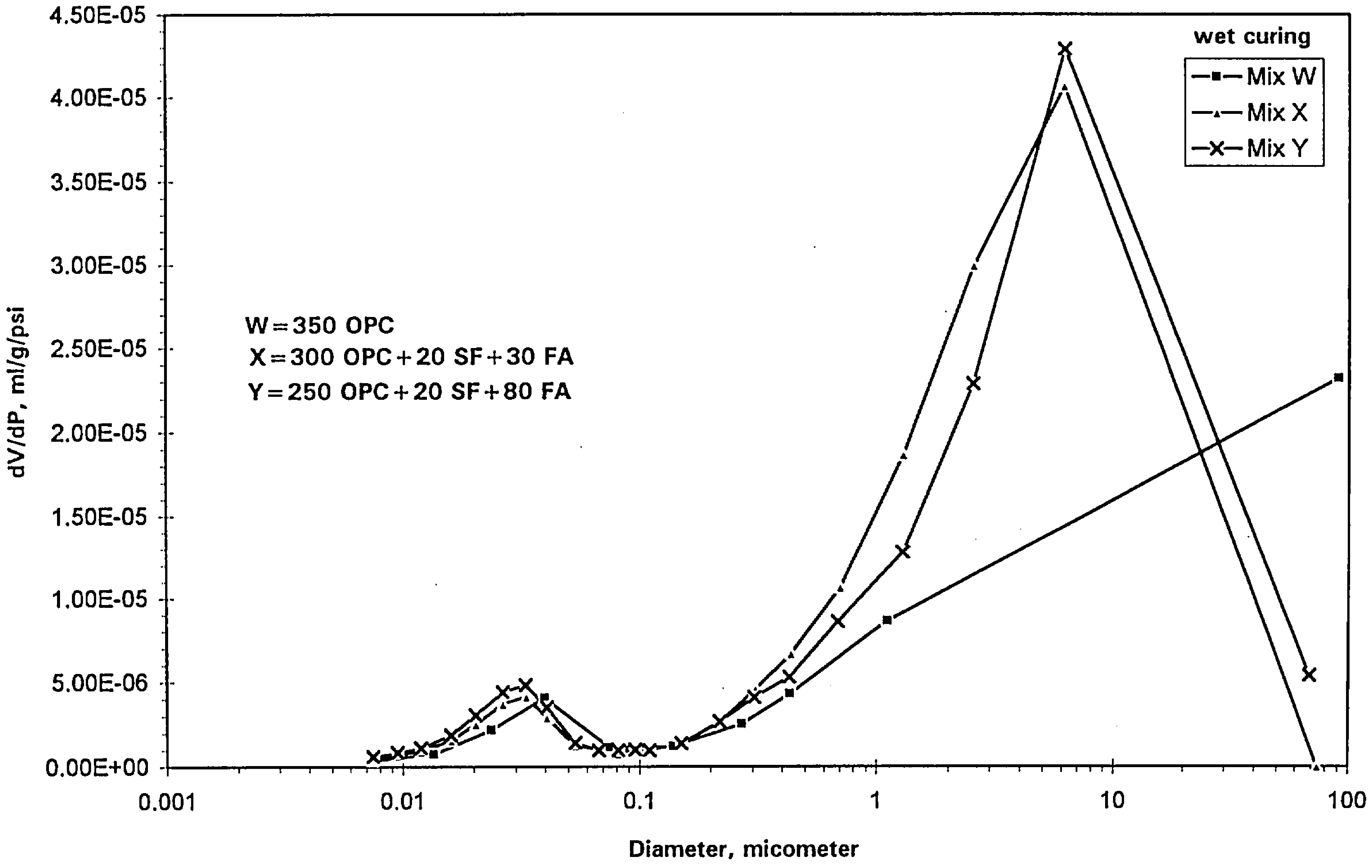


Figure 5.45 Influance of FA/SF on dV/dP varition

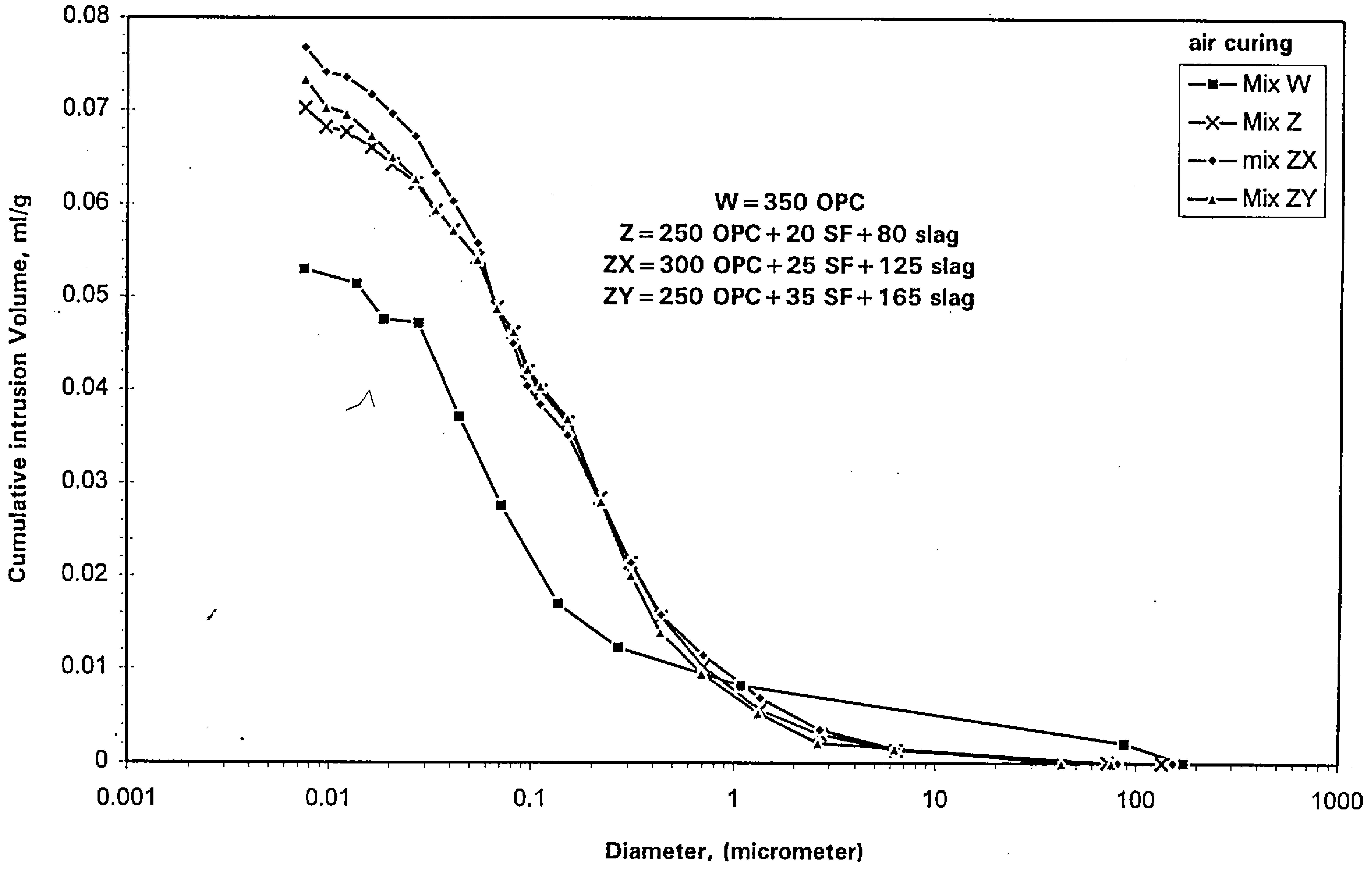


Figure 5.46 Influence of Slag/SF on pore size distribution

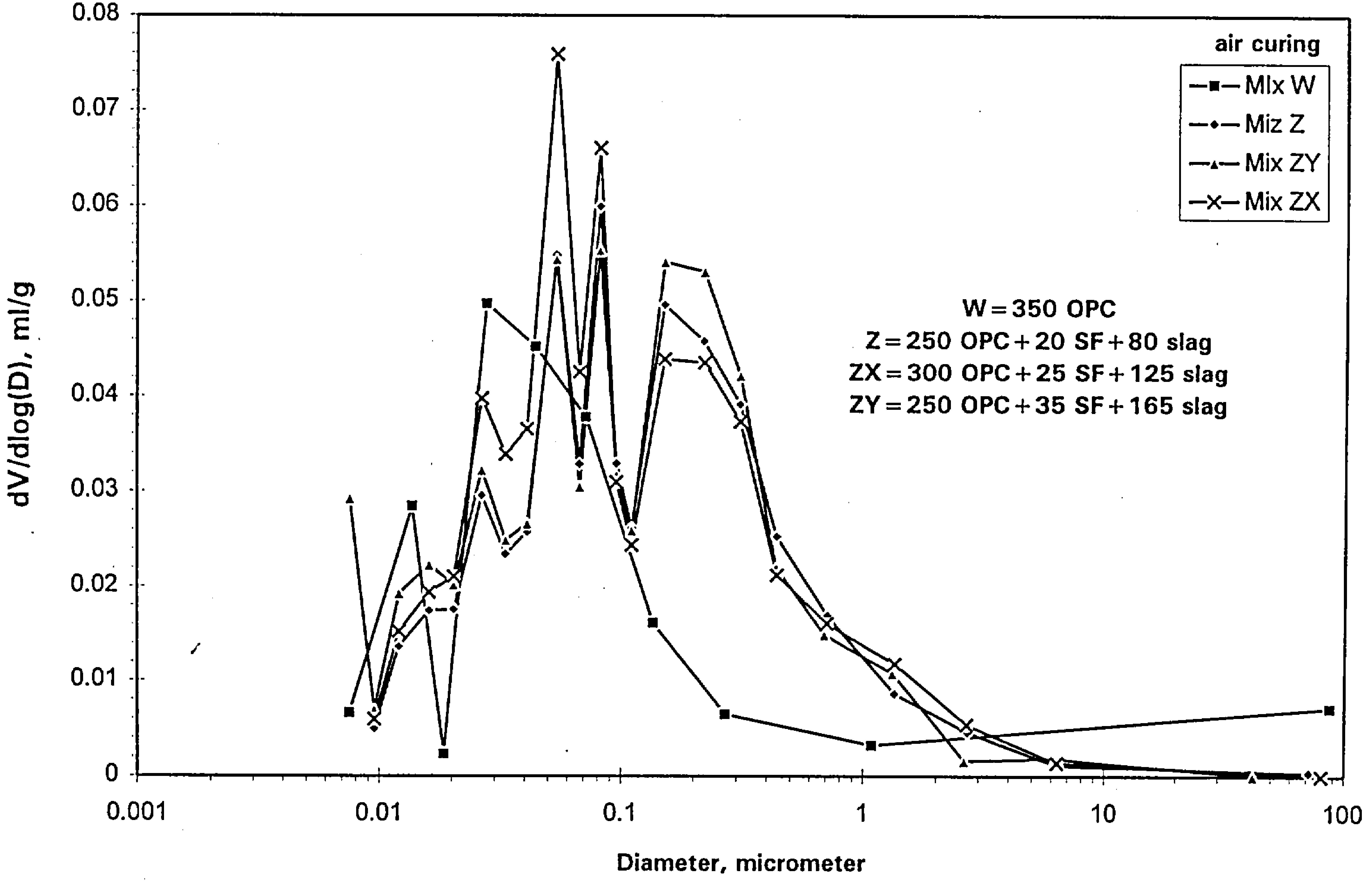


Figure 5.47 Influence of slag/SF on differential pore size distribution

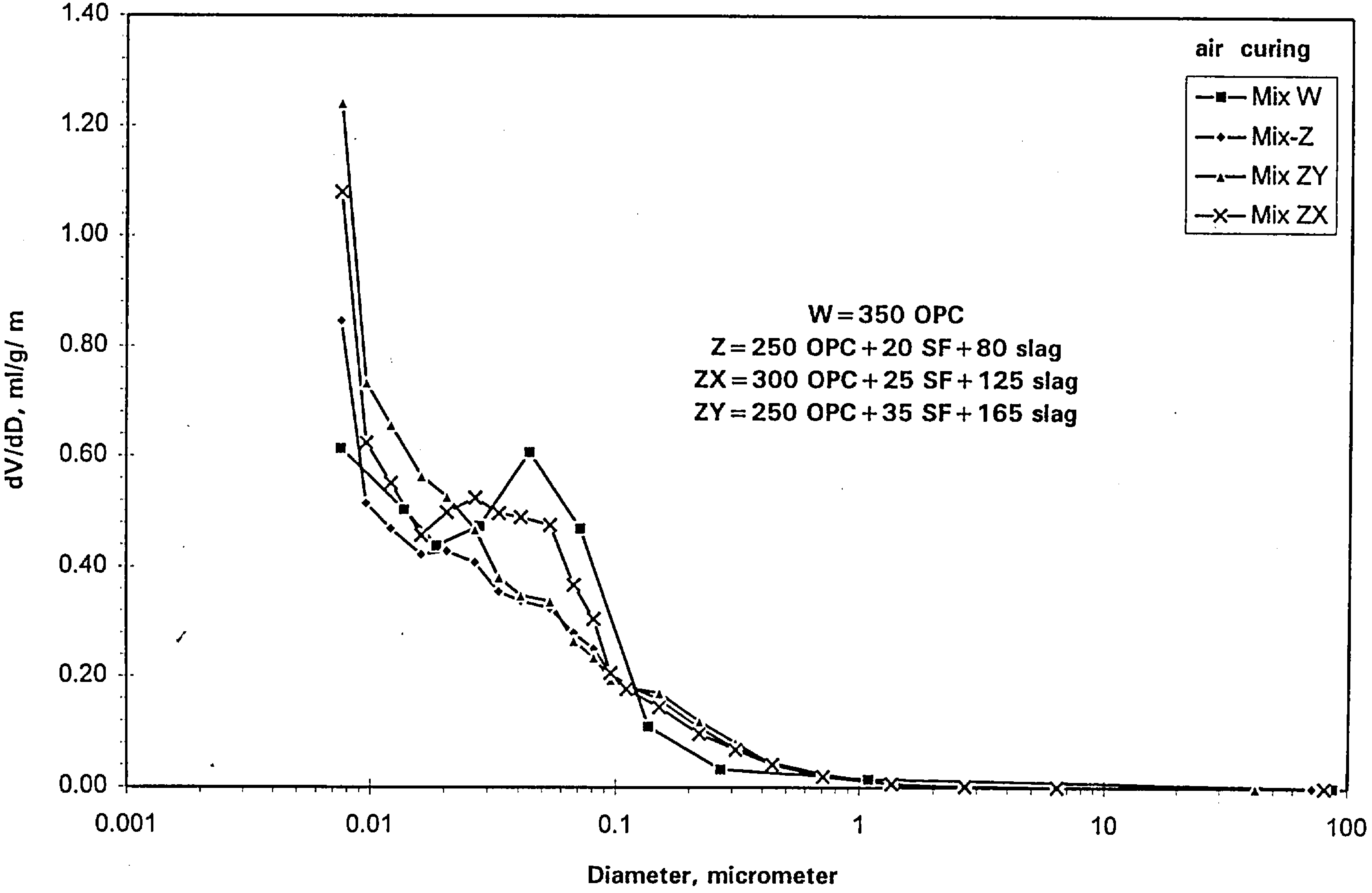


Figure 5.48 dV/dD vs. D curves for Control and slag/SF mixes

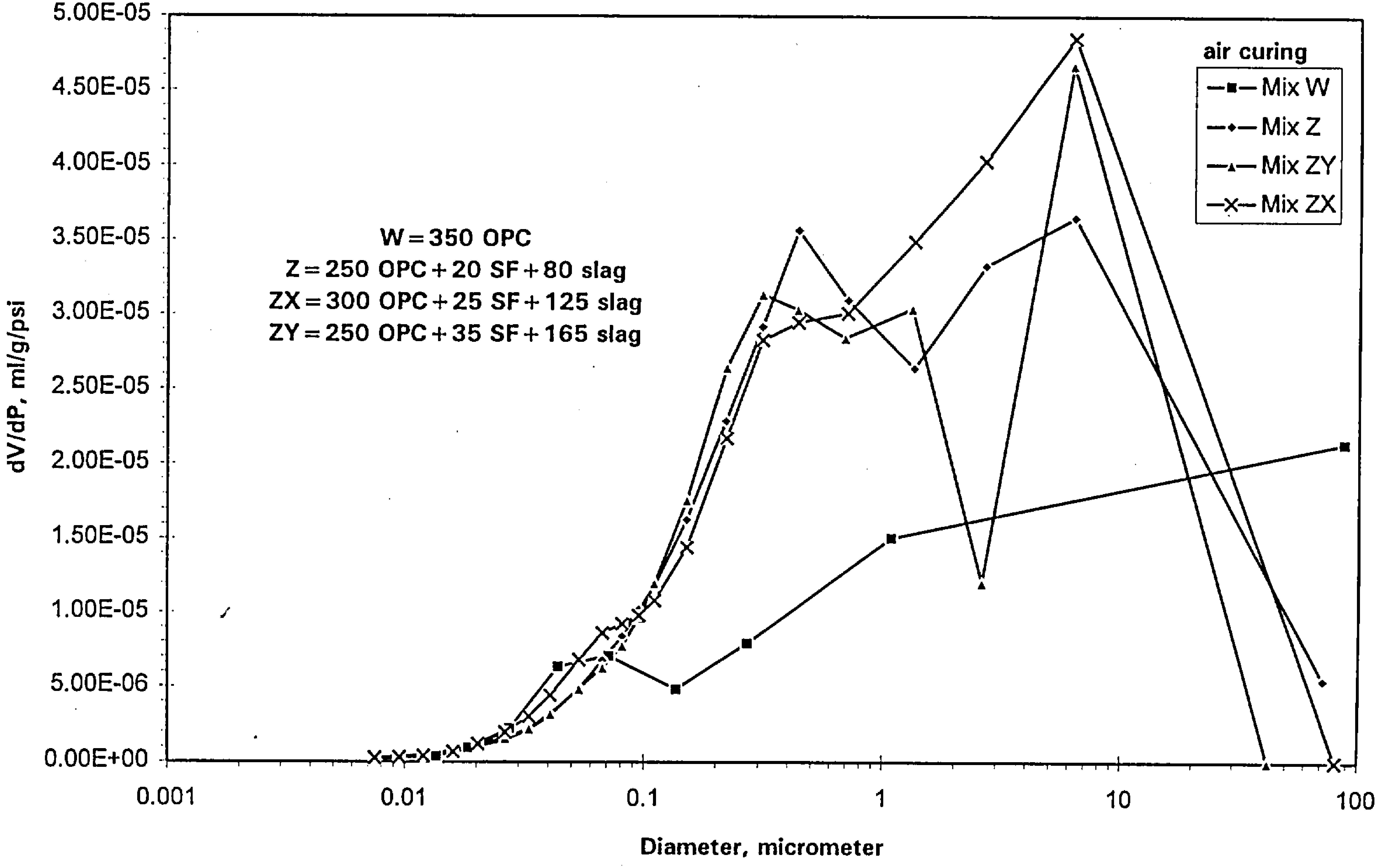
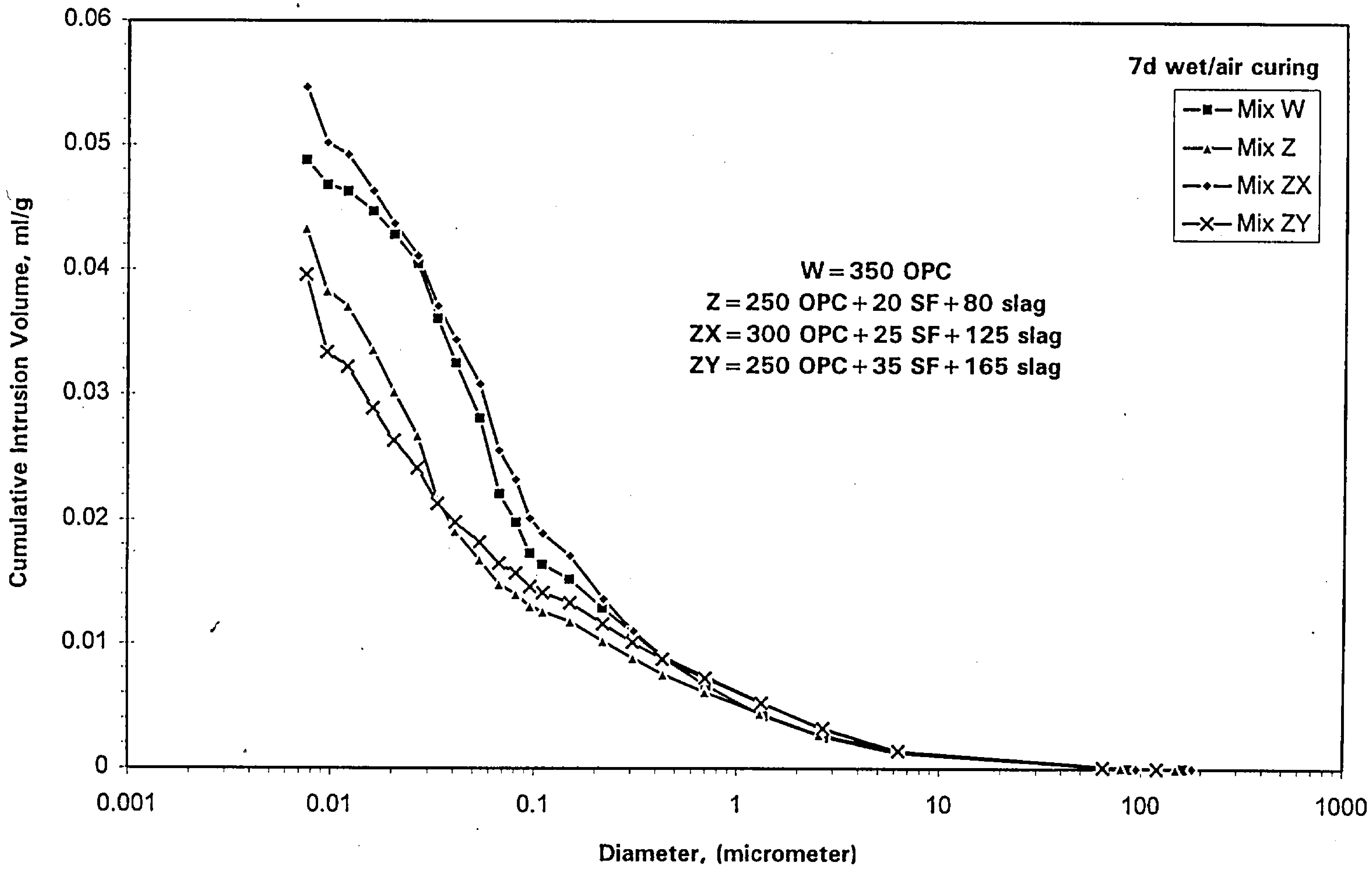


Figure 5.49 Influence of slag/SF on dV/dP variation



Figgure 5.50 Influence of Slag/SF on pore size distribution

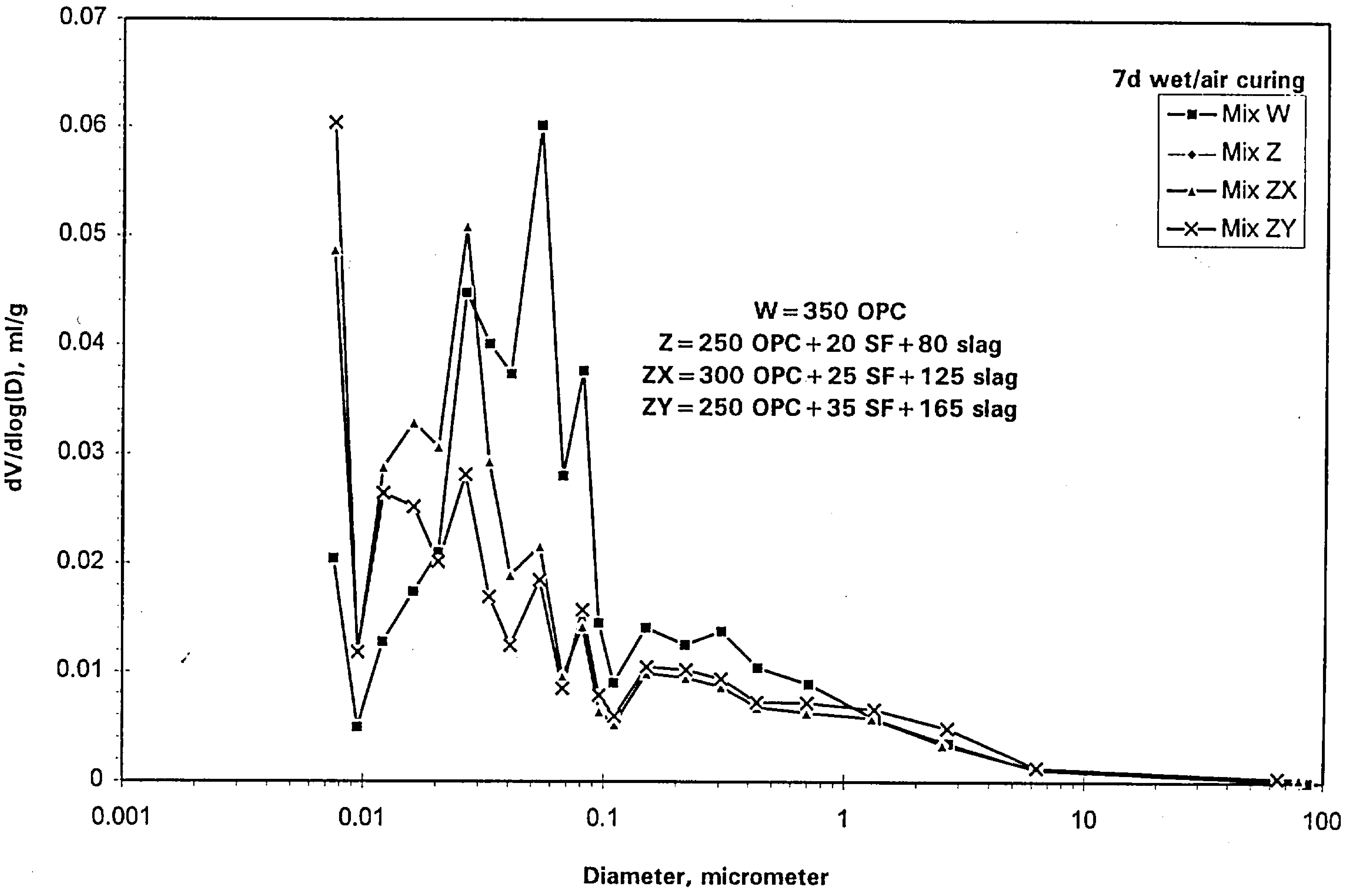


Figure 5.51 Influence of slag/SF on differetial pore size distribution

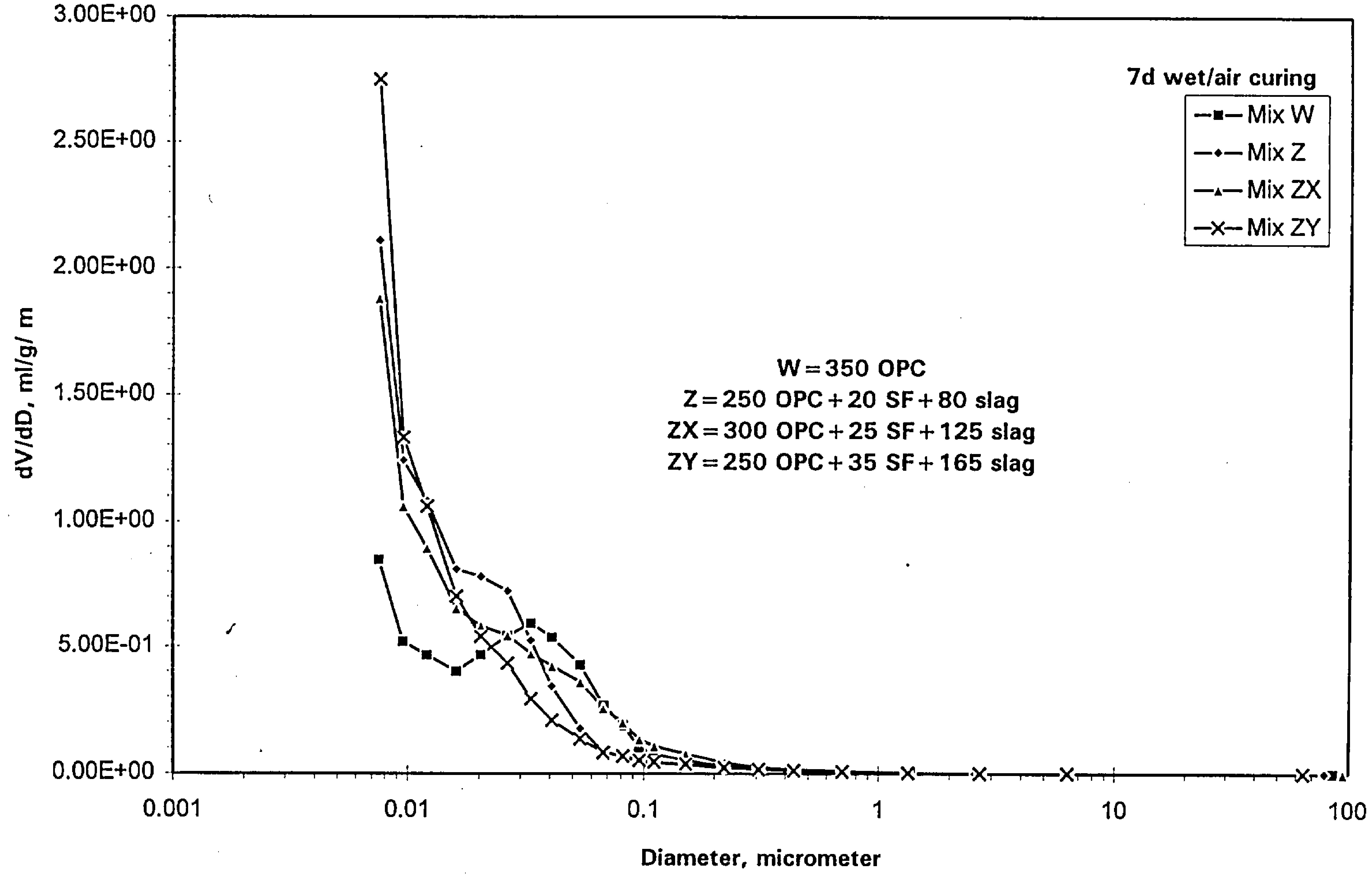


Figure 5.52 dV/dD vs. D curves for control and slag/SF mixes

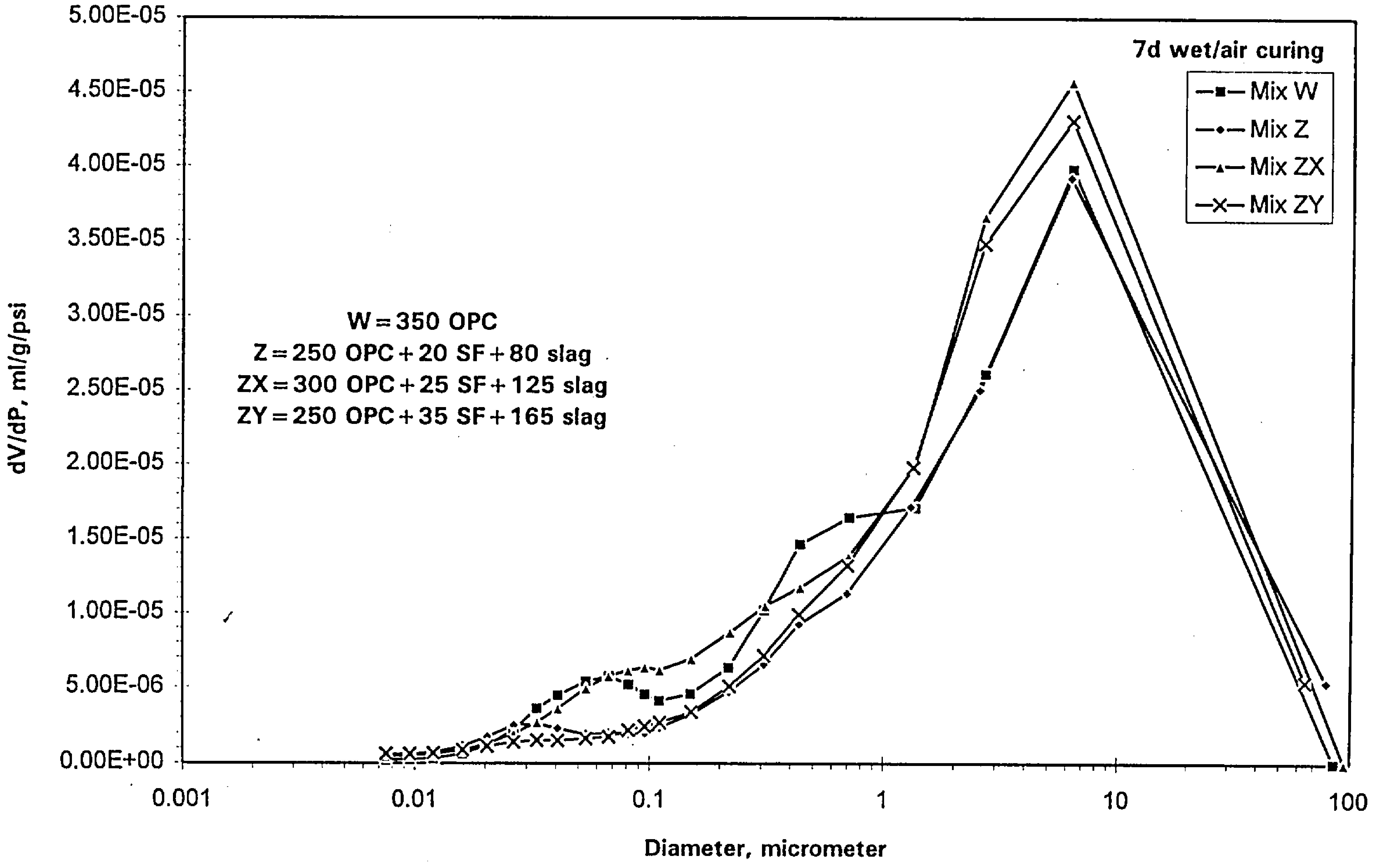


Figure 5.53 Influence of slag/SF on dV/dP variation

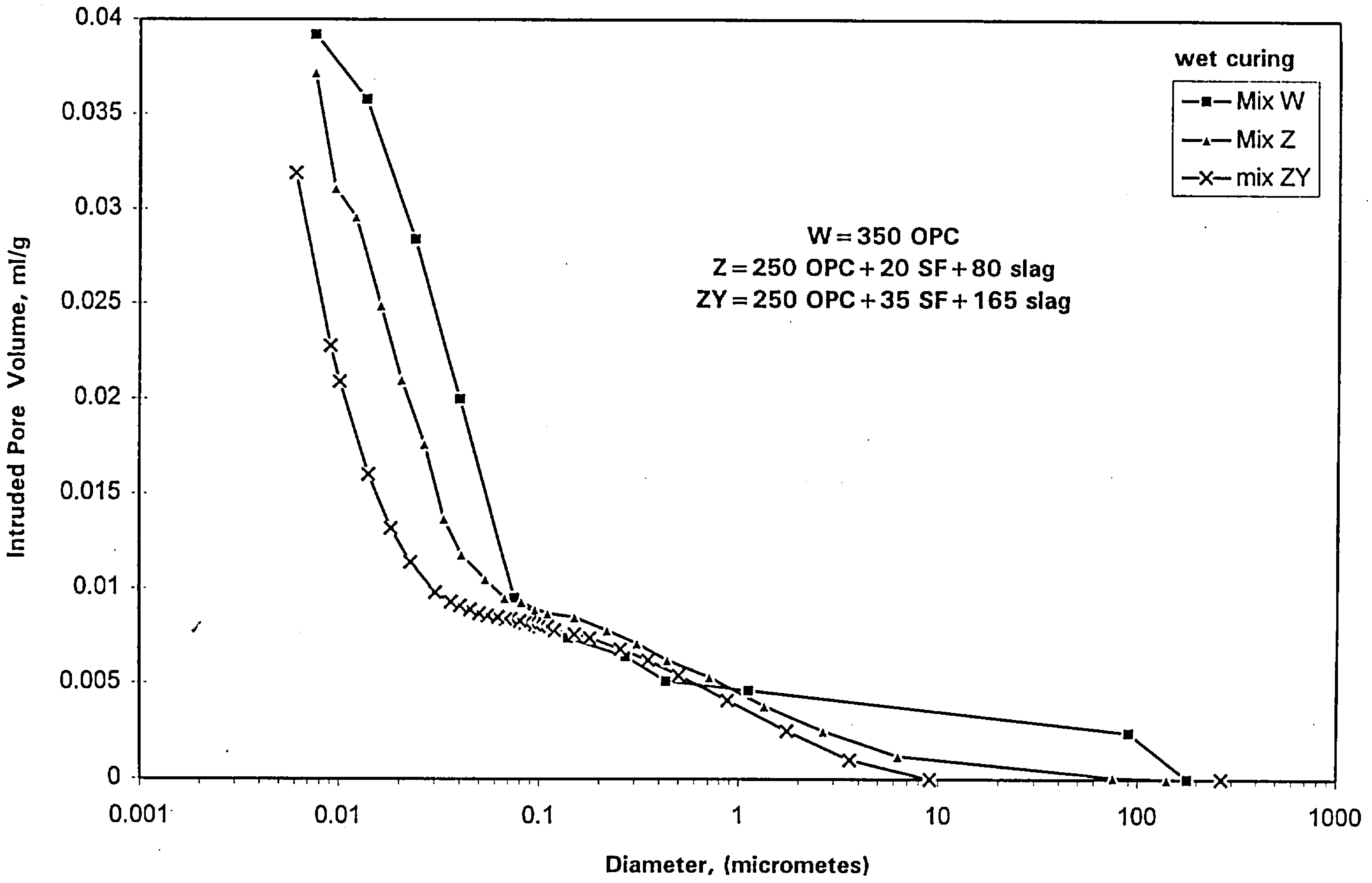


Figure 5.54 Influence of Slag/SF on pore size distribution

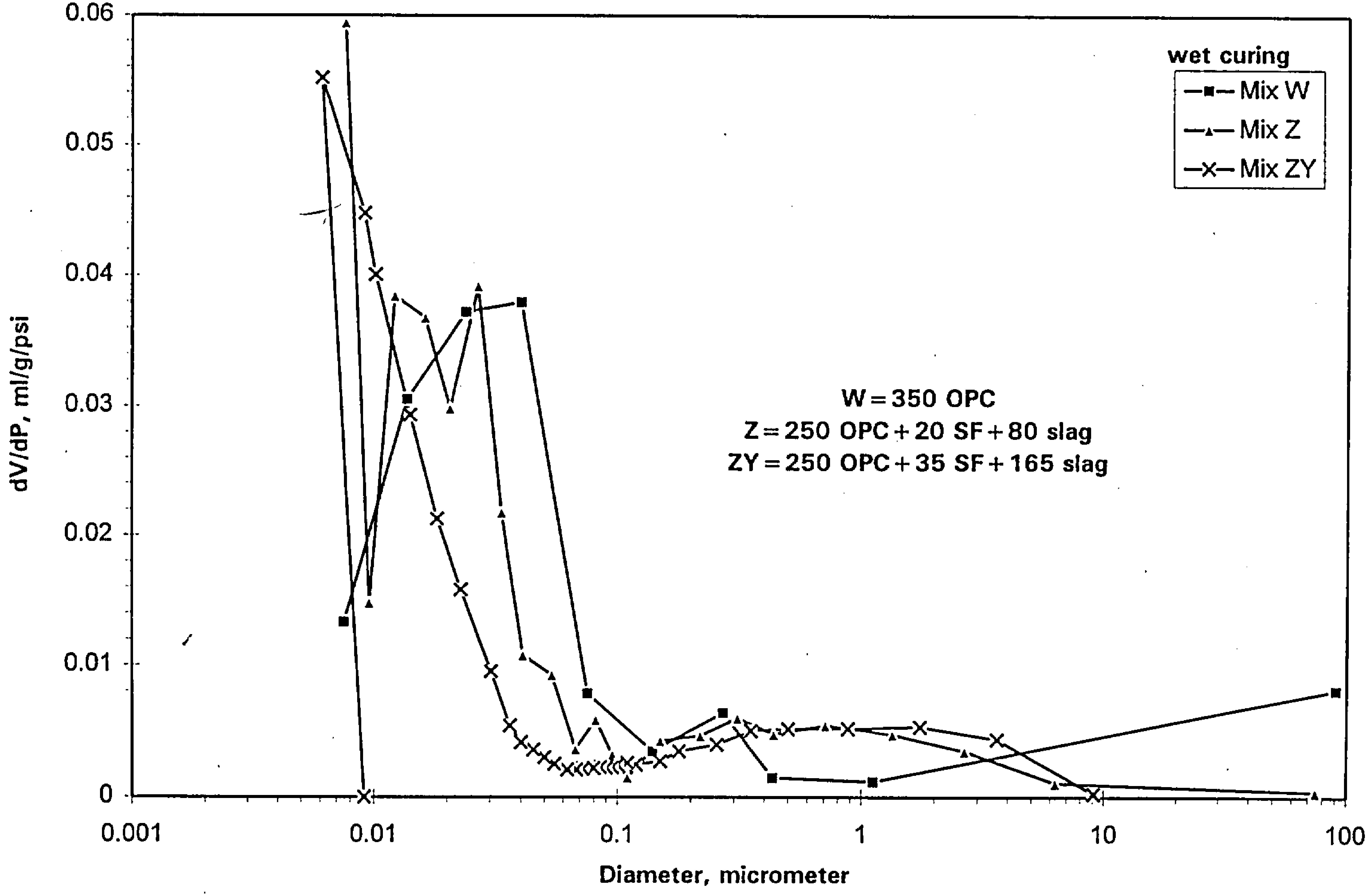


Figure 5.55 Influence of slag/SF on differential pore size distribution

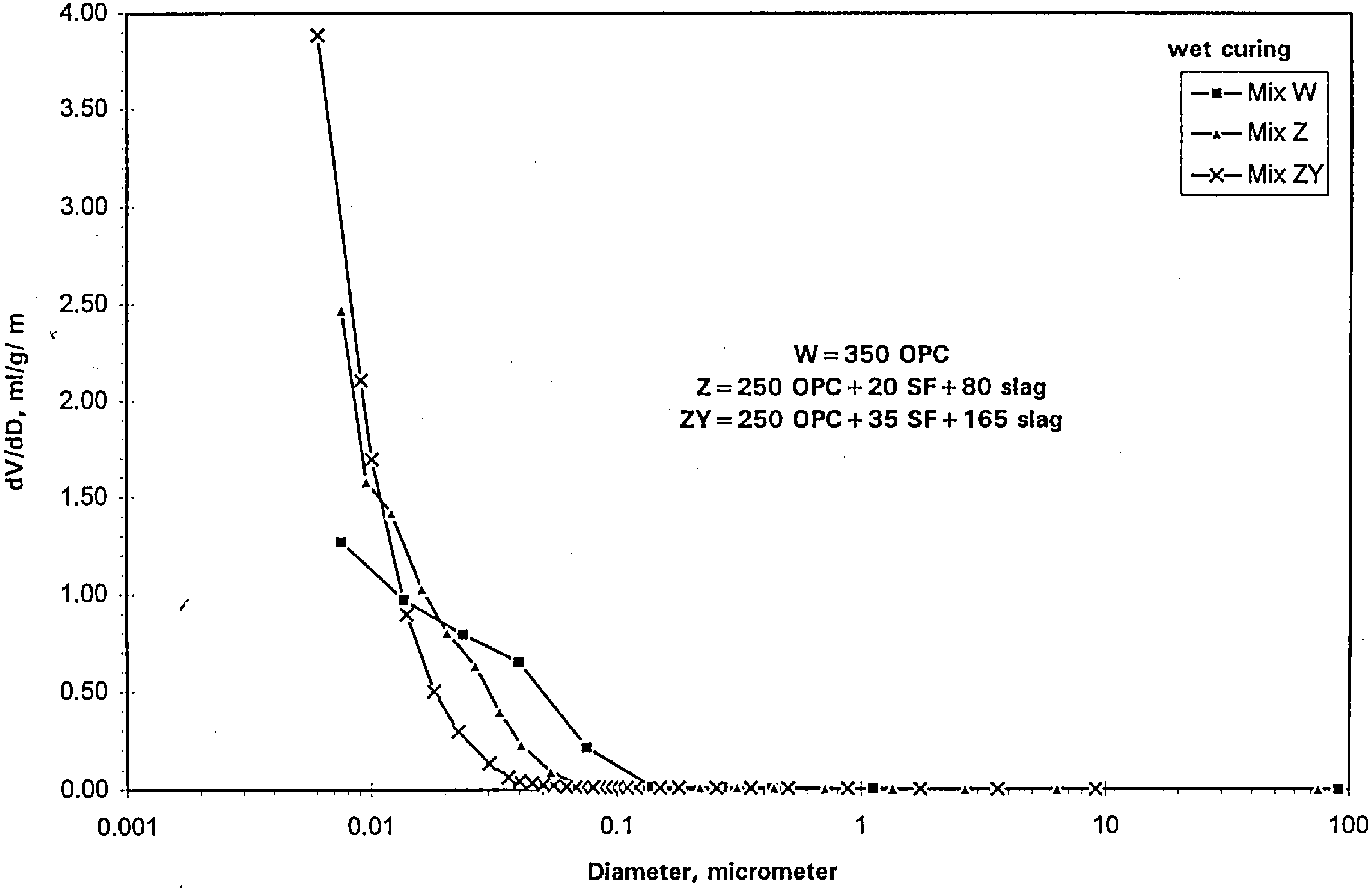


Figure 5.56 dV/dD vs. D curves for control and slag/SF mixes

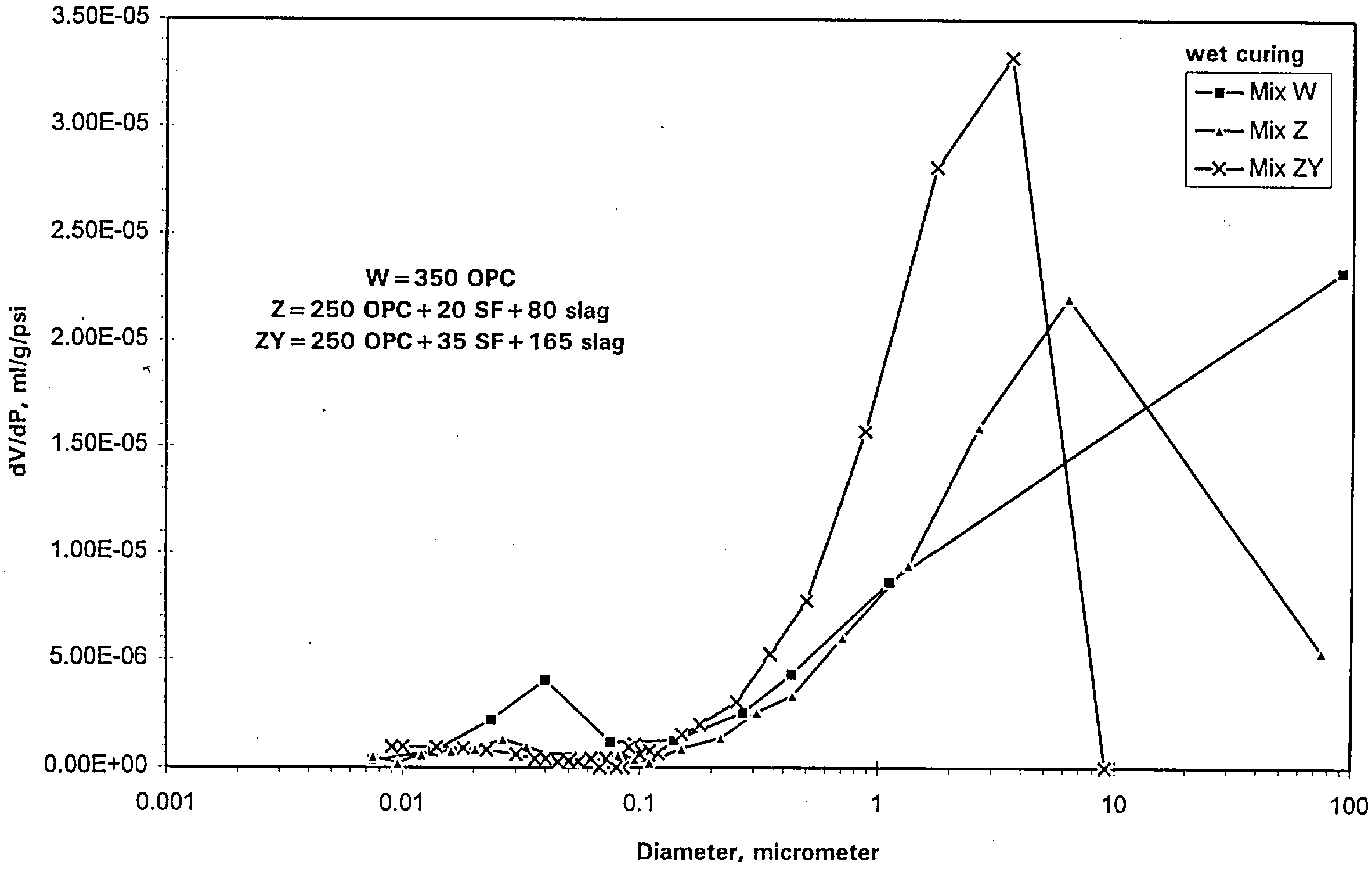


Figure 5.57 Influence of slag/SF on dV/dP variation

5.6 Relationship between Porosity and Compressive Strength

Many researchers have investigated the porosity/strength relationship for different concretes and hydrated cement pastes, and several equations have been suggested to express the relationships between porosity and strength.

Porosity compressive strength relationships for all concrete mixes investigated in this research were obtained. Figure 5.58 shows the graph representing this relationship. The equation based on this relationship for all concretes is:

$$y = 22.072 - 0.154x$$

where: y = total porosity (%)
x = compressive strength (MPa)

In general, there is good agreement between compressive strength and total porosity, as compressive strength increases the porosity reduces. From the figure it can be seen that the results could be grouped into two groups, one for the air-cured specimens and the other for wet- and 7d wet/air-cured specimens.

The porosity of all air-cured specimens are higher than wet- and 7d wet/air-cured specimens and fall above the regression line with the exception of the control mix, and this is due to insufficient curing water which possibly stopped the progress of hydration and the composition of the formed hydration products that fills the pores. However, with the exception of the control mix, porosity values of air-cured specimens are about the same, although they exhibited different compressive strength values (50 to 75 Mpa) i.e. mineral admixtured concretes of similar porosities can exhibit a wide range of compressive strengths, regardless of the cement replacement amount, depending on the curing. This means that under air-curing porosity could not be a function of strength and compressive strength could be a better indicator than porosity for quality of concrete.

On the other hand, wet-and 7d wet/air-cured specimens show how different concretes of different strengths can exhibit different porosities which might lead to different performances. The differences in the porosity of these concretes is believed to be due to the different cement replacement levels and curing conditions. It can be seen from Figure 5.58 that the decrease in the porosity of wet-and 7d wet/air-cured specimens of mix ZY results in lowering the porosity/strength relationship when compared with other concretes made with a similar water/binder ratio of 0.45 and when the correlation is lower, the lower the porosity.

However, the equation obtained should not be used as a general relationship since it is based on the results of a limited number of experiments. Furthermore, total porosity cannot describe pore characteristic, since at different cement replacement levels and curing conditions it varies widely. This reveals that in addition to the total porosity, the distribution of the pores would have an important role in the strength of concrete.

5.7 Relationship between compressive strength and large pores > 0.1 μm

The pore structure of cement paste is very important. It governs a series of properties of mortar and concrete such as: physical and chemical resistance, temperature resistance strength, thermal conductivity etc. [125]. The pore structure is changed by curing condition and cement replacement level, an effect which may be detected by using mercury porosimetry. As the compressive strengths and pore size distribution are determined by the concrete mixes investigated, these measurements are used to build up a relationship correlating the pore structure to the compressive strength. The large pores > 0.1 μm for the wet, 7d wet/air- and air-cured specimens are plotted against the corresponding compressive strength in Figures 5.59 and a linear relationship with a correlation coefficient of 0.60 is found to be

where $y = 0.076 - 0.01x$

y = large pores > 0.1 μm (ml/g)

x = compressive strength (MPa)

This linear relationship shows how the compressive strength and curing conditions affects the large pores of concrete. High compressive strength and better curing result in finer pore structures and vice-versa. It was expected that continuous wet-curing would increase the strength and bring refinement to pore structure, and that for the change of distribution of pore volumes (as shown in section 5.4) a coarsening of pores in the range > 0.1 μm due to air-curing is responsible. Figure 5.59 shows that this range has an important influence on the compressive strength. This is confirmed in all concrete mixes. Rostasy [125] reported that pores in the range ≥ 0.1 μm exerts a great influence on strength, and that strength is a function of the volume created by pores ≥ 0.1 μm .

It is interesting to know that although all concrete cured initially in water for 7 days had the same compressive strength as concretes subjected to continuous wet curing, the

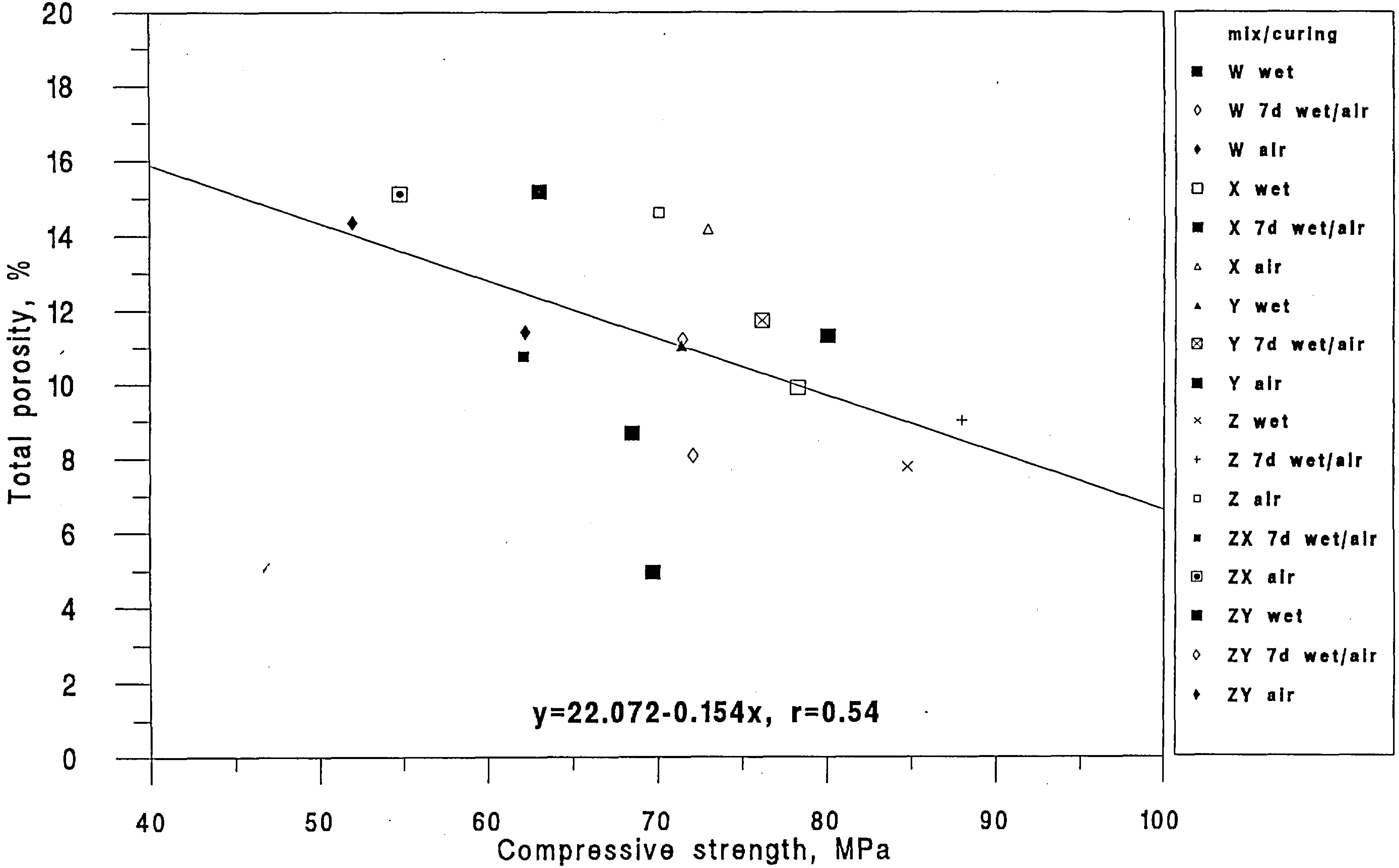


Figure 5.58 Relation between compressive stringth and total porosity

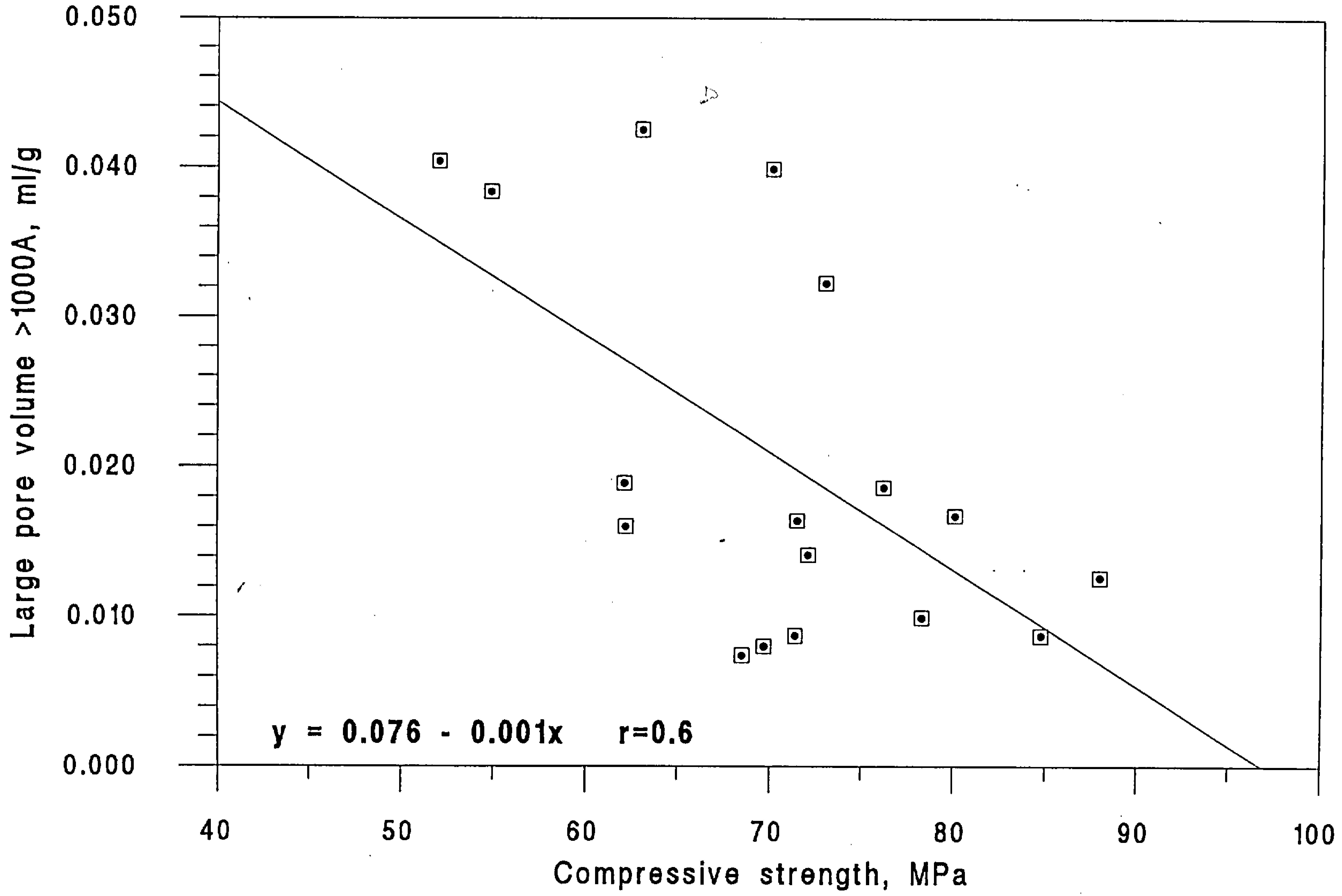


Figure 5.59 Relation between compressive strength and large pores>1000A

former exhibited higher large pore volume compared to the latter (with the exception of the control concrete), possibly due to that 7 day water-curing is not sufficient requirement needed for complete hydration for mineral admixtured concretes and a significant volume of large pores are not refined. This reveals that coarseness in pore structure could not be recognized by compressive strength values, and that except for the case of continued wet curing the compressive strength should not be used as a criterion of concrete quality. Since mechanical properties (dynamic modulus and flexural strength) and permeability vary quite differently from compressive strength when insufficiently cured mineral admixtured concrete begins to dry with time.

For a chosen pore volume the 7d wet/air- and wet-cured specimens of the control concrete shows a similar large pore volume. So one would expect that in general the plain Portland cement concrete will suffer a smaller loss of total pore volume due to insufficient curing than the mineral admixtured concretes.

5.8 Conclusions

For the concrete mixtures investigated and curing conditions employed, the following conclusions may be drawn:

1 The porosity and intruded pore volume of concrete specimens was found to be influenced by the curing regime, as well as by the type and replacement level of mineral admixtures.

2 The continuous wet curing of concrete is essential to achieve the lowest total porosity and fine pore structure.

3 The concretes which received no curing after demolding showed the poorest performance in terms of strength development, porosity and pore size distribution. The insufficient hydration of cement and pozzolanic materials is likely to be responsible for such poor performances. However, the concretes wet-cured for 7 days showed significant improvement in strength, pore structure and other characteristics compared with concretes without any curing.

4 Air-cured specimens yielded higher porosity values and coarser pore structure compared with continuously wet-cured specimens. The intruded pore volume of FA/SF air-cured specimens was about 40% larger than that of the wet-cured

specimens, while the intruded pore volume for slag/SF concretes was about twofold under air-curing relative to continuous curing.

5 Subjecting the concretes to 7 days of wet curing, relatively improved the pore structure of control, FA/SF and slag/SF blended mixes, and the total porosity values were lower than those obtained in air-curing conditions. Under this curing, the slag/SF blended mixes showed better performance than the FA/SF blended mixes i.e. lower porosity and lower total pore volume. The results, however, showed that water-curing in the early stage of concrete is essential and has an important role in the improvement of pore structure and other characteristics and hence the durability.

6 Continuous water-curing improved the pore structure of all concretes and produced significant reductions in the threshold diameters. The threshold diameters of slag/SF concretes were the lowest in this curing condition, while they were the highest in air-curing.

7 Under continuous water-curing, concrete with 165 kg/m^3 slag replacement yielded the lowest porosity and pore volume, whilst the 80kg/m^3 FA concrete exhibited the largest porosity and pore volume.

8 The addition of FA increased the intruded pore volume of specimens under the three curing conditions used in this study. The intruded pore volume increased with increasing the amounts of FA.

9 The finer pore structure was not observed in the concrete containing the FA. Under both 7d wet/air-curing and water-curing conditions, the large pore ($D > 0.1$ μm) volume of concretes containing FA was a little larger than that of the control mix specimen. Under air-curing conditions, their large pore volume was much larger than the control mix concrete.

10 The concretes containing FA had a smaller threshold diameter than control mix under water-curing conditions. Under 7d wet/air-curing conditions, their threshold diameters were the same as that of the control mix. However under air-curing, their threshold diameters were much larger than that of the control mix.

11 Replacing 30 and 80 kg/m^3 of cement by FA resulted in increased porosity and pore volume for the curing regimes employed in this research.

12 Replacing 125kg/m^3 of cement by slag yielded about the same porosity and total pore volume as that of the 30kg/m^3 FA mix, however, they were slightly higher than the 165kg/m^3 slag mix.

13 Replacing 80 and 165 kg/m^3 of cement by slag reduced the porosity and pore volume compared with the control and other mixes for continuous water and 7d wet/air-curing regimes, but had high pore volume and coarser pores compared to the control mix when there was no water curing.

14 The compressive strength was found to be inversely related to the total porosity. This relationship is influenced by the presence of cement replacement materials in concrete and the type of curing.

15 A good relationship was found between the large pores >1000A and the compressive strength which reveals that prolonged drying results in a coarser pore structure and lower strength, whereas finer pore structure and higher strength will be obtained for more wet-cured concrete.

16 The above mentioned results have clearly shown that additions of slag and SF caused pore refinement or transformation of larger pores into fine pores. The pore refinement, however, only occurs in both continuous water-curing and 7 day water/air-curing conditions. Under air-curing conditions, the pore coarseness increased in concretes containing slag. This clearly emphasizes the importance of proper curing of concrete containing slag.

CHAPTER SIX

TEST RESULTS AND DISCUSSIONS OF PART III
OXYGEN PERMEABILITY

6.1 Introduction

One of the important parameters influencing the durability of concrete is its permeability. Permeability of concrete may be defined as the ease with which the deleterious substances can penetrate the concrete. It is also related to the degradation caused by the freezing and thawing since it controls the ease with which concrete can be saturated with water [31]. Although of direct relevance to the durability of concrete, there is no British Standard specification for a pressure-induced permeability test [126] or limiting values of permeability as criteria for designing concrete [13]. This is because it is difficult to specify one permeability test to cover the various environmental conditions to which concrete may be exposed (i.e. the different degrading agents and mechanism by which they penetrate concrete, and also because of the difficulty of conditioning concrete samples before testing, since moisture content influences the results to a great extent [9,127].

There are many different tests to establish the permeability of concrete. Many of these tests do not measure the permeability directly, but produce a 'permeability index' which is related to the method of measurement. However, permeability is usually defined in terms of basic physical properties (such as, intrinsic permeability or coefficient of diffusion) [9]. These tests are discussed by the Concrete Working Party Report [9].

Permeability of blended cement concrete to air or gases is of interest in structures. Mineral admixtures have been traditionally used to improve such property and to reduce costs by replacing cement with low-cost industrial by-products. Although research on permeability of blended cement concretes started a few decades ago. The literature available on the gas permeability of concrete containing combinations of cementitious system is littel. Improvement in the strength, modulus of elasticity, pulse velocity and shrinkage of concrete containing 20 to 35 kg/m^3 SF (by mass of cementitious material) and either FA or slag as an additional mineral admixture led to this study on the role of supplementary cementitious components in concrete permeability. The results on strength and other engineering properties have been reported in Chapter 4, including the production of 90 Mpa concrete.

This chapter deals with the influence of continuous wet, 7d wet/air and air curing on air permeability of concrete mixes made with various practicable range of combinations of FA/SF and Slag/SF blends. The air permeability of concrete was carried out by a new gas permeameter designed by Cabrera and Lynsdale [13]. The air permeability of concrete was estimated by means of the coefficient of air permeability.

6.2 Air permeability test

The determination of the permeability of a sample of a porous medium consisted of conducting a laboratory flow test and applying Darcy's law to the resulting data. The test itself consisted of flowing the fluid of interest through the sample at various rates and recording the flow rates and appropriate pressures.

6.2.1 Theory

Many of the studies have evaluated the air permeability as well as water permeability by means of the coefficient of permeability [129]. Although the calculation of coefficient of air permeability varies with the test method and shape of specimen, the concept of the coefficient of air permeability obeys Darcy's Law:

$$v = \frac{kA\Delta P}{\mu l} \qquad (6.1)$$

where ν = flow rate (cm^3/s)
A = cross-sectional area of specimen (m^2)
l = length of specimen (m)
ΔP = fluid pressure head across specimen (bar)
μ = viscosity of fluid ($N.s/m^2$)
k = intrinsic permeability (m^2)

When a compressible fluid, such as oxygen, is used, D'Arcy's equation is modified, and the permeability coefficient obtained is normally defined by the equation [13,64,129]:

$$k = \frac{2P_2Vlx2.02x10^{-6}}{A\left(P_1^2 - P_2^2\right)} \qquad (6.2)$$

where P_1 = absolute applied pressure (bar)
P_2 = pressure at which the flow rate is measured, usually 1 bar.

For a cylindrical specimens of 50 mm diameter and 30 to 40 mm length with oxygen of 2.02×10^5 N.s/m^2 viscosity, one bar pressure is applied to the top surface of the specimen for half an hour to allow a steady state flow rate. The gas flow rate through the specimen is measured by means of a bubble flowmeter of which the diameter is 1.7mm and the bubble rise height is 10 cm. However, equation (6.2) can be reduced to:

$$k\left(m^2\right) = \frac{157.574 x l(m) 10^{-16}}{time(\sec)} \qquad (6.3)$$

The intrinsic permeability (k) has a unit of area and is dependent on properties of the porous media only since the viscosity of the fluid is included in this equation, unlike the co-efficient of permeability which has a unit of velocity and is dependent on both properties of the fluid and the porous media [9].

This equation has been used to evaluate the oxygen permeability of various concrete specimens cured under different conditions.

6.2.2 Apparatus

The air permeability testing equipment (cell) used in this investigation for determining the intrinsic permeability was developed by Cabrera and Lynsdale [13].

A schematic diagram of the cell is shown in Figure 6.1. Figure 6.2 shows a battery of four cells and Figure 6.3 shows in detail the components of a cell for testing concrete specimens.

The permeability cell consists of a sample holder, accurate pressure gauge, stable gas supply and a flow-meter at the downstream side. The cell works on the same principle as that of the Cement and Concrete Association cell [71,130], but the method by which the sample is confined laterally in order to ensure one directional flow is different. The size of the cell, and consequently the size of the sample tested, is also different. The cell has been designed to test either mortar specimens of 25mm diameter and 10 to 50 mm height or concrete specimens of 50 mm diameter and 10 to 50 mm height.

Gas is forced to flow only in the vertical direction by placing the sample (B) in a rubber cylinder (A) (see Figure 1) inside a steel ring cylinder (C), so that when a vertical force is applied on the assembly, through the cap of the cell (H), the rubber cylinder is forced

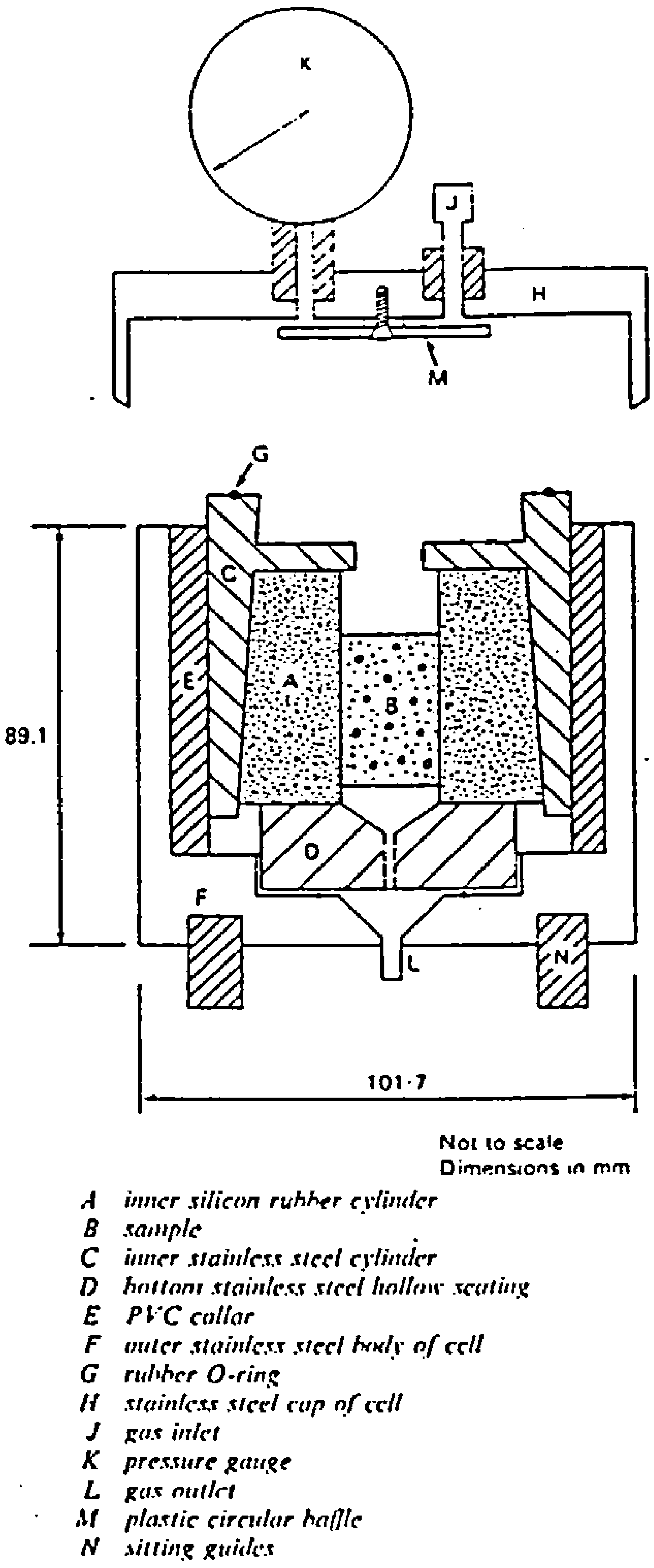


Figure 6.1 Schematic diagram of the permability cell [13]

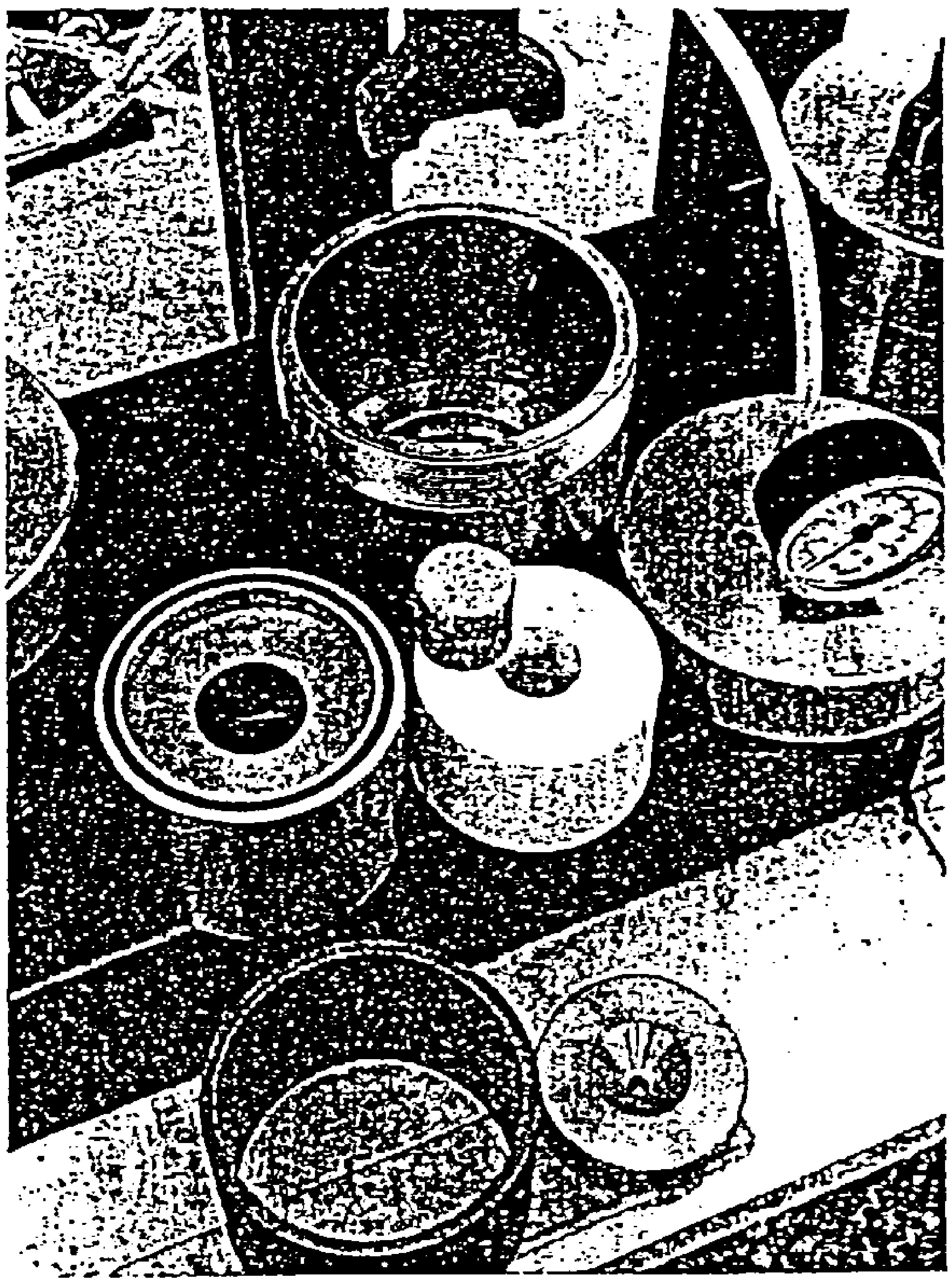


Figure 6.3 The components of the permeability cell used [13]

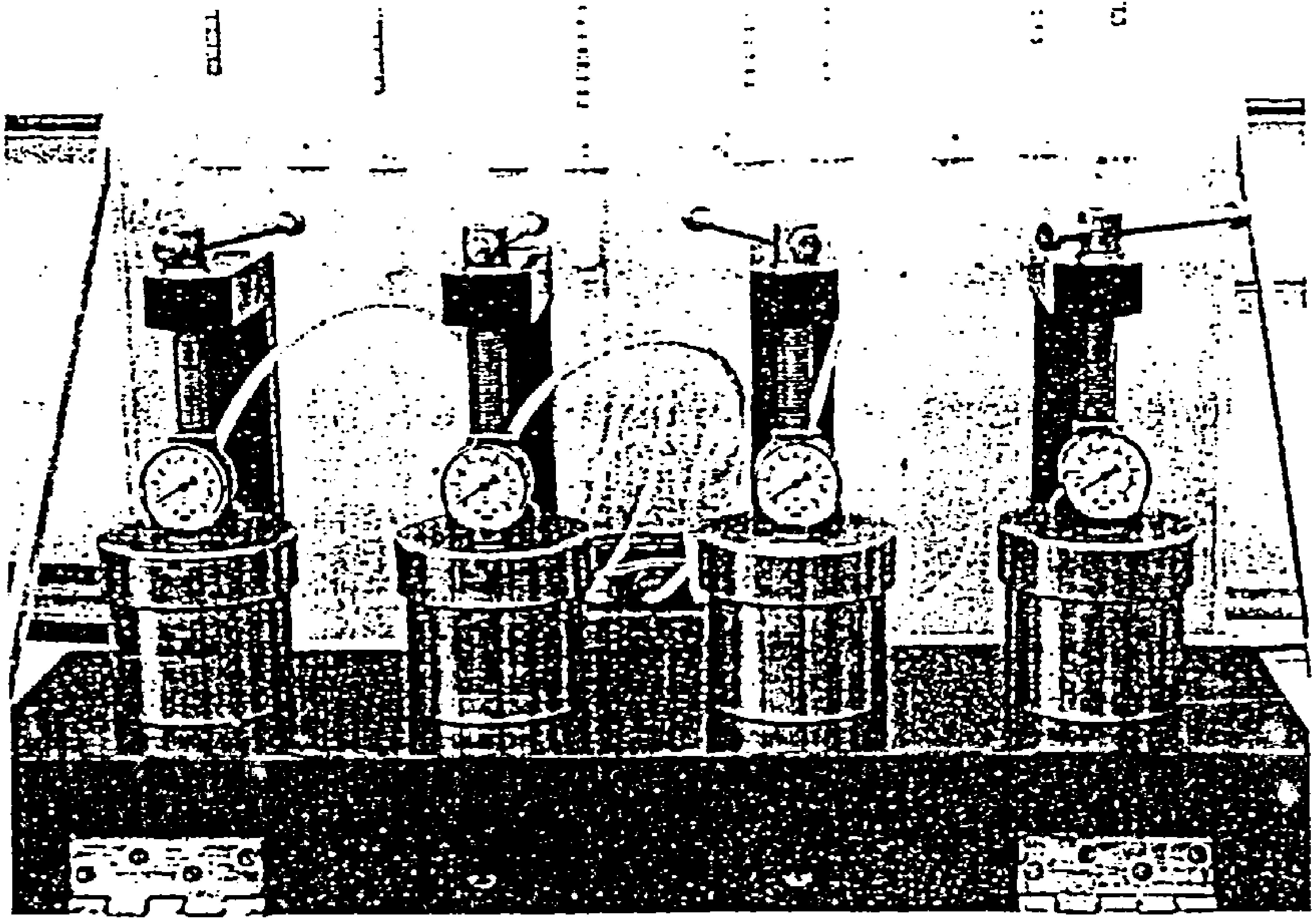


Figure 6.2 General view of the permeability cells in use [13]

inwards against the sample and thus provides a seal. Full details are given in reference [13].

The test is considered to be an easy and fast technique for determining the permeability of concrete. It can be used to obtain permeability profiles through the depth of a concrete element in order to evaluate the influence of different curing conditions or curing compounds [131]. The above permeability cell was later modified by Cabrera to measure water permeability as well.

6.2.3 Preparation of specimens

Concrete specimens were used for the permeability test, although most of the tests described by researchers do measure permeability on mortar samples and consider them to be an adequate model for that in concrete, and this may be questionable.

Six different concrete mixes were used in this investigation, mixes W,X,Y and Z of total cement content of 350 kg/m^3 and mixes ZX and ZY of total cement content of 450kg/m^3, similar to those studied in chapter four and five. The water/binder ratio for all mixes was kept constant, 0.45. Superplasticiser (SP6) was added to all mixes. The manner in which the concrete was mixed is similar to that mentioned in chapter 3. A minimum of three 100 x 100 x 500 mm prisms were cast in a steel mould for each mix. After casting, the specimens were covered by polythene sheets in order to eliminate evaporation. After demoulding, which was done the next day, the concrete specimens were exposed to one of the following curing conditions for periods of 7, 120 and 240 days.

1) Continuous water-curing (specimens were referred to as wet-cured)
2) No water-curing (specimens were referred to as air-cured)
3) 7 days water-curing followed by exposure to internal lab environment (specimens were referred to as 7d wet/air-cured).

When the specimens were required for testing at these ages, the concrete prisms were taken out of the curing environment and cored by 50 mm coring bit to obtain the required samples for oxygen permeability testing. The cores were sliced using a diamond saw into cylinders of 32-40 mm in height. In the case of top slices, 10 - 15 mm were removed from each core to avoid any effect on the permeability measurements as shown in Figure 6.4. The coolant for both coring and slicing was water. All the specimens cored were dried in an oven at 105± 5°C for approximately 44 hours until constant weight was reached. This eliminates any possible variation of the results due to the

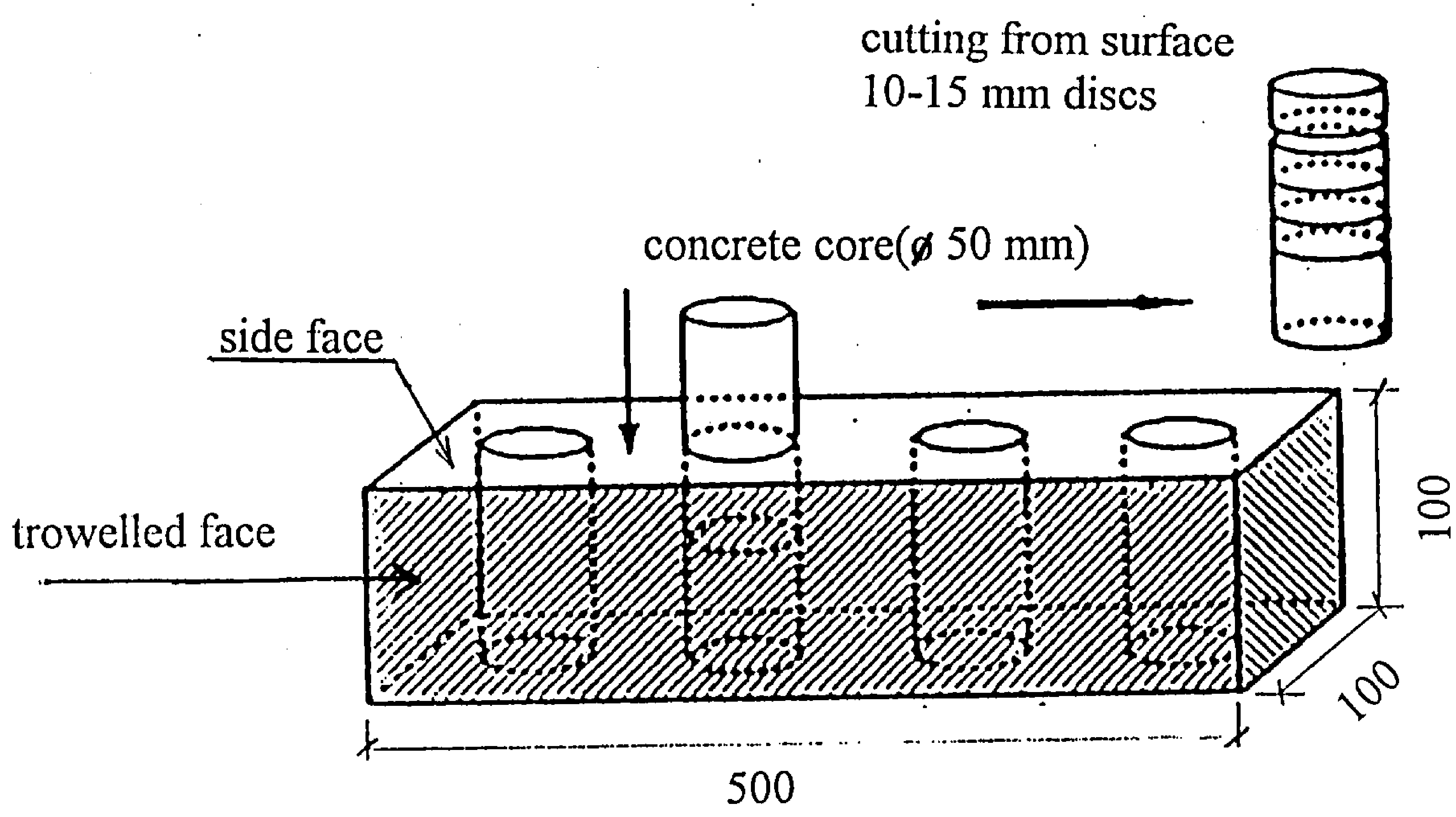


Figure 6.4 Schematic diagram of a concrete specimen extracted for permeability test.

residual moisture within the specimens while testing. Air permeability measurements can be very sensitive to the level of moisture within concrete [126], and could block the passage of gas through certain routes and, as a result, lower permeability values would be obtained. On the other hand, severe (i.e. complete) drying (e.g. at 105°C [132]) may result in shrinkage cracking and modification of the pore structure may lead to unreal permeability values [13]. Generally, it is accepted that the gas permeability increases as the drying temperature increases. However, for the discussion carried out in section 5.3.3, and recommendation of many researchers in this field it was decided to adopt the 105°C oven drying method for conditioning specimens prior to testing. This has the advantage of giving a short conditioning period for a test specimen, a simplified test procedure, a high flow rate with dry specimens and, an improved reproducibility of test results [133]. The oven-dried specimens were then cooled to room temperature in an air-tight container (desiciator) for at least 2 hours before being tested for oxygen permeability.

6.3 Influence of curing

The values of intrinsic permeability for the different concrete cores which were cured under continuously wet, 7d wet/air and air conditions, and tested at different ages (7, 120 and 240 days) are shown in Table 6.1 and Figures 6.5 to 6.13. Each value represents the average of four specimens. The trends obtained from the permeability measurements, were as expected similar to those obtained from measurement of the pore size distribution. These results reveal the changes in the performance-related properties of badly cured concrete due to insufficient hydration. This high variation in permeability values of different cured specimens is attributed to the sensitivity of mineral admixtures used in concretes to prolonged drying.

6.3.1 Effect of age

The increase of oxygen permeability with age is demonstrated in all the 7d wet/air- and air-cured specimen results gathered in this investigation. Generally it is accepted that permeability would decrease with age as a result of increased hydration leading to the reduction and discontinuity of the large pores as they become filled with hydration products. Contrary to the trend for hardened concrete, the oxygen permeability of concretes increase with age. Similar trends were found by other researchers [69,71,129,134]. However this effect was higher between 7 and 120 days permeabilities than that between 120 and 240 days. It was difficult to attribute specific reasons as to the increases in oxygen permeability measurements, but some of the following points could help to explain the reasons:

- Many researchers determine air permeability measurements on cement paste or mortars rather than concrete where aggregate volume concentration is present. Generally, aggregates in cement paste affect permeability [135]. Powers [136] suggested that aggregates reduce the effective area of flow, increase the flow path length and introduce fissures and cracks around the particles in mortar, allowing increased permeability. Norton and Pletta [137] presented data to indicate that increasing the volume concentration of aggregate increases permeability of mortar composite. Nyame [135] concluded that aggregates can have two opposing influences upon permeability, size and volume obstructions to flow can reduce permeability whilst interfacial effects and aggregate properties can increase the permeability of a composite. He also concluded that the permeability increases as porosity reduces. Some of the results reported here are in agreement with this conclusion.

- In contrast to the effect of curing on compressive strength, where it was found that water-curing for 7 days or air-curing (i.e. drying) did not effect strength gain, permeability increased with age. With the increase of drying the coefficient of air permeability increases as part of capillary cavities become paths for air flow [129]. Nagataki and Ujike also concluded that the coefficient of air permeability not only depends on mixture proportions, but is also affected by the degree of drying. For every mixture, when concrete is saturated with water, concrete actually has air tightness. After that, air begins to flow through concrete when the water in the capillary cavities is evaporated by drying. Because the evaporation of water in the capillary cavities is dependent on drying conditions, the change of air permeability of concrete is also dependent on drying conditions. It appears that microcracks in a concrete base has much more effect on air permeability than pore structures of mortar in concrete. Trapped air in concrete also affects the air permeability of concrete, as air content increases the co-efficient of air permeability increases. In water permeability of concrete, it has been reported that water flows through air voids when high water pressure acts upon concrete [129]. In regard to air permeability of concrete, it is considered that air voids also become part of the path of air flow when water in the capillary cavity is evaporated by drying [129].

- Complete drying (conditioning specimens at 105°C) may result in shrinkage cracking which modifies the pore structure, leading to artificially high permeability values [13].

Measurements of samples pre-dried at different temperatures (20, 50, 80, and 105°C) show that gas permeability increases as the drying temperature increases [132].

6.3.2 Influence of curing

Curing conditions to which a specimen is subjected have a significant influence on its permeability and pore structure. As stated earlier, three curing conditions were adopted in this investigation. A wide range of results for oxygen permeability in different curing conditions is presented in this section. All the permeability values discussed are to the power 10^{-16}.

The intrinsic permeability values for the control mix (W) under different curing conditions and at different ages are presented in Figure 6.7 and Table 6.1. Consistently, the air-cured specimens displayed the highest oxygen permeability, followed by 7d wet/air cured specimens and wet-cured specimens at all ages of curing. For example, at the age of 7 days the permeability values of wet-and 7dwet/air-cured specimens were about the same, 0.461 and 0.474m² compared with 0.622m² for air-cured specimens. At the age of 120 days, the permeability of 7d wet/air- cured specimens was close to that of air-cured ones, whereas the wet-cured specimens permeability was, 0.279m², about half of both 7d wet/air- and air- cured one. At 240 days, all the specimens under the three curing conditions showed only very slight change in the permeability compared with their 120 days value. Their ranking was still the same (i.e. wet <7d wet/air <air). This shows that 7 day water, curing for early age might be enough, but not for later ages, and that with no curing the permeability would be more than double that of wet-cured specimens.

If mix X is considered in Figure 6.8, the oxygen permeability at 7 days for wet and 7d wet/air- cured specimens was about the same, 0.264 and 0.289m² respectively, compared with 0.410m² for air-cured specimens which was 45 to 55% higher than those for wet and 7d wet/air-cured specimens. At 120 days, both 7d wet/air- and air-cured specimens, permeability increased by 28% whereas in the case of wet-cured specimens the permeability slightly decreased to 0.246m², and then increased to 0.396m² at 240 days. At this age, both 7d wet/air- and air-cured specimens registered permeability of 0.452 and 0.638m², respectively, showing an increase of 20 and 55% on their 7 and 120 days values. Again both 7d wet/air- and air-cured specimens permeabilities were higher than those for wet cured ones.

Considering mix Y specimens in Figure 6.9, it can be seen that air cured specimens exhibited the largest oxygen permeability at all ages, followed by 0.962 and 0.846m² for

7d wet/air-cured specimens at 7 and 240 days respectively. The difference in permeability values at these ages is not so great as the wet-cured specimens which gave the minimum value of $0.416m^2$. At 240 days, the 7d water/air and air cured specimens permeability was twice and three times that of the wet-cured specimens, respectively.

Figure 6.10 presents results of oxygen permeability of mix Z. The various curing regimes used are clearly indicated on each of these figures. The differences in permeabilities between 7, 120 and 240 days varied under the three curing conditions. The wet-cured specimens yielded the smallest permeability values, 0.157, 0.298, and $0.311m^2$ at 7, 120 and 240 days, respectively. There was an increase in permeability between 7 and 120 days but, it was not significant between 120 and 240 days age values, and this could be due to the oven drying effect that might have resulted in shrinkage cracking which modifies the pore structure, leading to a high permeability value. Similarly, an increase in permeability of wet-cured specimens with age was found by another researcher [134], and he attributed that to oven drying effect.

The oxygen permeability of 7d wet/air cured specimens was 0.231, 0.314 and $0.518m^2$ compared with corresponding values of 0.537, 0.561 and $0.778m^2$ for air cured specimens at 7, 120, and 240 days, respectively. This shows that specimens which were not cured at all in water at an early age have a greater coefficient of permeability of air than those initially 7 day cured with water. The increase in these values from the age of 7 days to 240 days is small, because the specimens are dried at very early ages. The specimens cured in water until the age of 7 days shows small values for coefficient of permeability of air but increasing value from 7 days to 240 days. The reason is that specimens 7d wet/air cured sufficiently in water have more moisture to evaporate, and denser structure because of more hydration than air-cured specimens. Kasai et al. [69] show the same permeability to air behaviour for OPC, FA/OPC and slag/OPC 7 day water and no water cured specimens at the age of one month to three months, as shown in Figure 6.11. They also attributed this to the presence of more water in the 7d water cured specimens. However, air cured specimens permeability was badly effected, and was 150% and 50% higher than wet- and 7d wet/air-cured specimens at the end of the curing period.

Table 6.1 and Figure 6.12 shows the permeability results of mix ZX under 7d wet/air and air-curing conditions. Similar conclusions could be drawn for this mix also. The oxygen permeability of 7d wet/air- and air-cured specimens increased by about 40 and 35%, respectively, from 120 to 240 days, which means that the drying effect was slightly higher for 7d wet/air-cured specimens, but the absolute permeability values for 7d wet/air-cured specimens where lower than the air-cured ones.

If mix ZY is considered in Figure 6.13, the trend in permeability for the 7d wet/air- and air-curing conditions is similar to the trend obtained for the above discussed mixes, but the effect of drying is more pronounced on this mix. The wet-cured specimens at 120 days yielded a permeability of 0.381m^2 compared with 1.185 and 1.938 m^2 for 7d wet/air- and air-cured specimens, respectively. The differences in these values are great. For the 7d wet/air- and air-cured specimens, permeabilities were threefold and fivefold that of the wet ones, respectively. This obviously indicates the importance of curing especially for mixes of high cement replacement materials, and the effect of drying which is more critical compared with other mixes. However, the increase in permeability of 7d wet/air- and air-cured specimens from 120 day to 240 days was about 45 and 30% respectively.

6.4 Influence of cement replacement materials

In this section the oxygen permeability of FA/SF and slag/SF concretes is compared with control OPC concrete, and the effects of replacement of FA and slag are studied. The coefficients of permeability determined for different cured concrete cores cut from concrete prisms are given in Table 6.1 and Figures 6.14 to 6.22.

6.4.1 Oxygen permeability of concrete mixed with FA/SF

Figures 6.14-6.16 and Figures 6.17-6.19 shows the effect of replacement of FA and SF on oxygen permeability. In the case of water-curing for 7 days, the value of co-efficient of permeability of concrete containing 30kg/m^3 FA and 20kg/m^3 SF is lower by 40% than that of the control concrete without cement replacement materials. However, when the replacement level of FA is 80kg/m^3 (i.e. mix Y), the permeability is larger than that of the control. Values of 0.461, 0.264, and 0.901m^2 were obtained for mixes W, X and Y respectively. At age of 120 days under continuous water-curing, the permeability of the three mixes W, X and Y was low and close to each other, as if the mixes were independent of the replacement amount of FA. They had the permeability values of 0.279, 0.246, and 0.298m^2, respectively.

At this age the permeability has the minimum value with both FA replacement levels. It could be due to the fact that capillary cavities were filled up by hydrated compounds due to pozzolanic reaction which takes place during the continuous curing in water for 120

Tabel 6.1 Oxygen permability values for the different cured concretes at different ages (x 10^{-16} m^2)

Mix type	Continous water curing			7 day water / air curing			Air curing		
	7 day	120 day	240 day	7 day	120 day	240 day	7 day	120 day	240 day
350 OPC (W)	0.473 0.450	0.256 0.270 0.280 0.311	0.269 0.298 0.292 0.307	0.490 0.457	0.596 0.589 0.592 0.597	0.642 0.583	0.760 0.666 0.541 0.522	0.661 0.641	0.649 0.679
AVERAGE	0.461	0.279	0.291	0.474	0.593	0.613	0.622	0.651	0.664
300 OPC +20 SF +30 FA (X)	0.275 0.254	0.267 0.310 0.217 0.191	0.392 0.397 0.398 0.396	0.271 0.307	0.425 0.444 0.306 0.293	0.559 0.353 0.497 0.397	0.324 0.366 0.486 0.466	0.637 0.624 0.466 0.382	0.613 0.664
AVERAGE	0.264	0.246	0.396	0.289	0.367	0.452	0.410	0.527	0.638
250 OPC +20 SF +80 FA (Y)	0.853 0.950	0.289 0.302 0.308 0.294	0.370 0.492 0.421 0.379	0.965 0.960	- - - -	0.788 0.904	1.536 1.568 1.024 0.942	- - - -	1.396 1.211
AVERAGE	0.901	0.298	0.416	0.962	·	0.846	1.267	·	1.304
250 OPC +20 SF +80 Slag (Z)	0.174 0.140	0.262 0.308 0.306	0.305 0.324 0.304	0.222 0.239	0.310 0.318	0.492 0.545	0.551 0.635 0.471 0.493	0.435 0.518 0.640 0.651	0.787 0.811 0.755 0.758
AVERAGE	0.157	0.292	0.311	0.231	0.314	0.518	0.537	0.561	0.778
300 OPC +25 SF +125 Slag (ZX)	- - - -	- - - -	- - - -	- - - -	0.674 0.656 0.472 0.514	0.734 0.861	- - - -	1.144 0.876	1.448 1.284
AVERAGE	·	·	·	·	0.579	0.798	·	1.01	1.366
250 OPC +35 SF +165 Slag (ZY)	- - - -	0.401 0.327 0.416	- - - -	0.690 0.714 0.884 0.876	1.15 1.22	1.727 1.670	1.179 1.132 1.098 1.144	2.035 1.842	2.45 2.51
AVERAGE	·	0.381	·	0.791	1.185	1.698	1.138	1.938	2.48

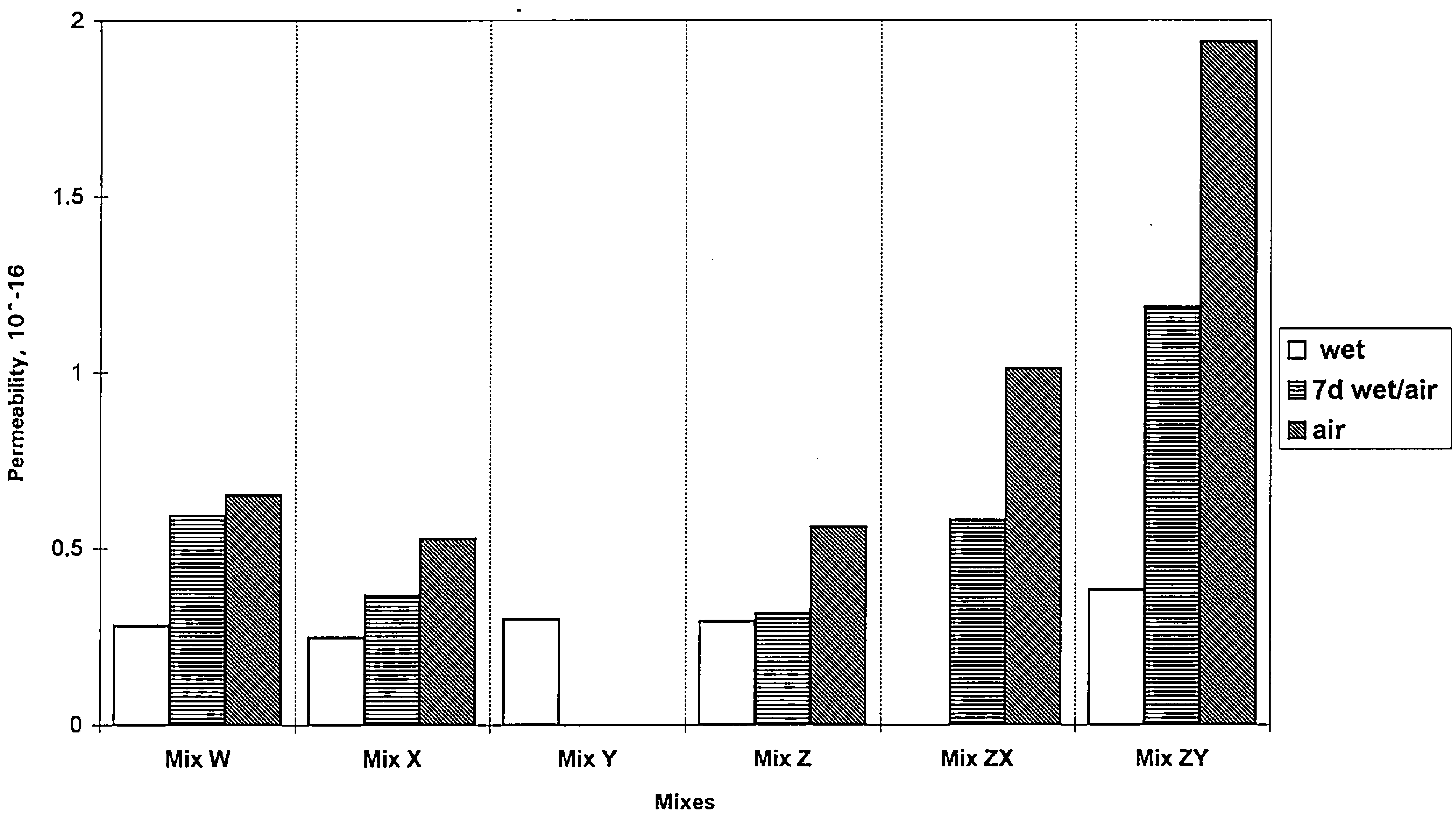


Figure 6.5 Permeability under different curing conditions at 120 days age

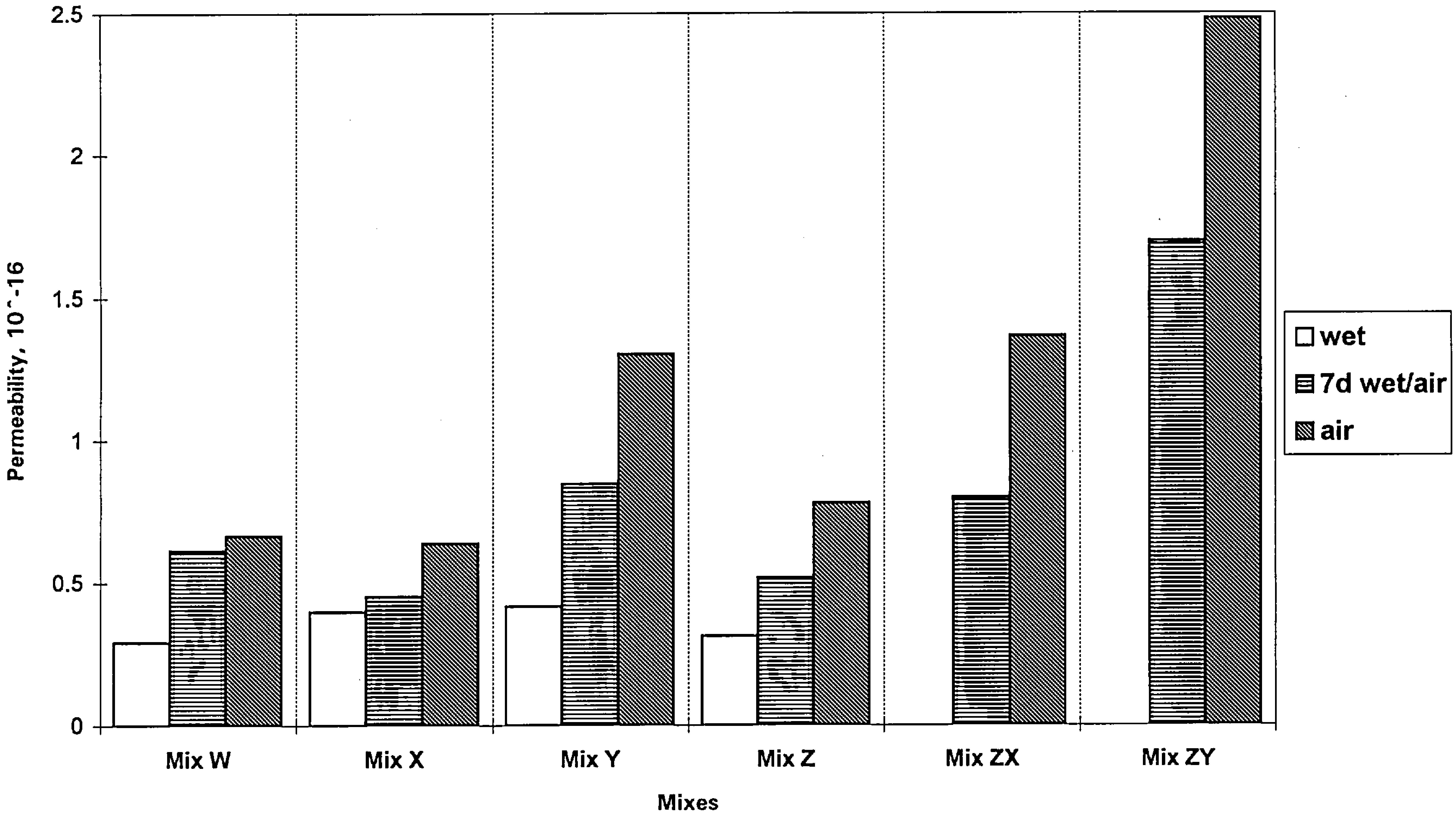


Fig 6.6 Permeability under different curing conditions at 240 days age

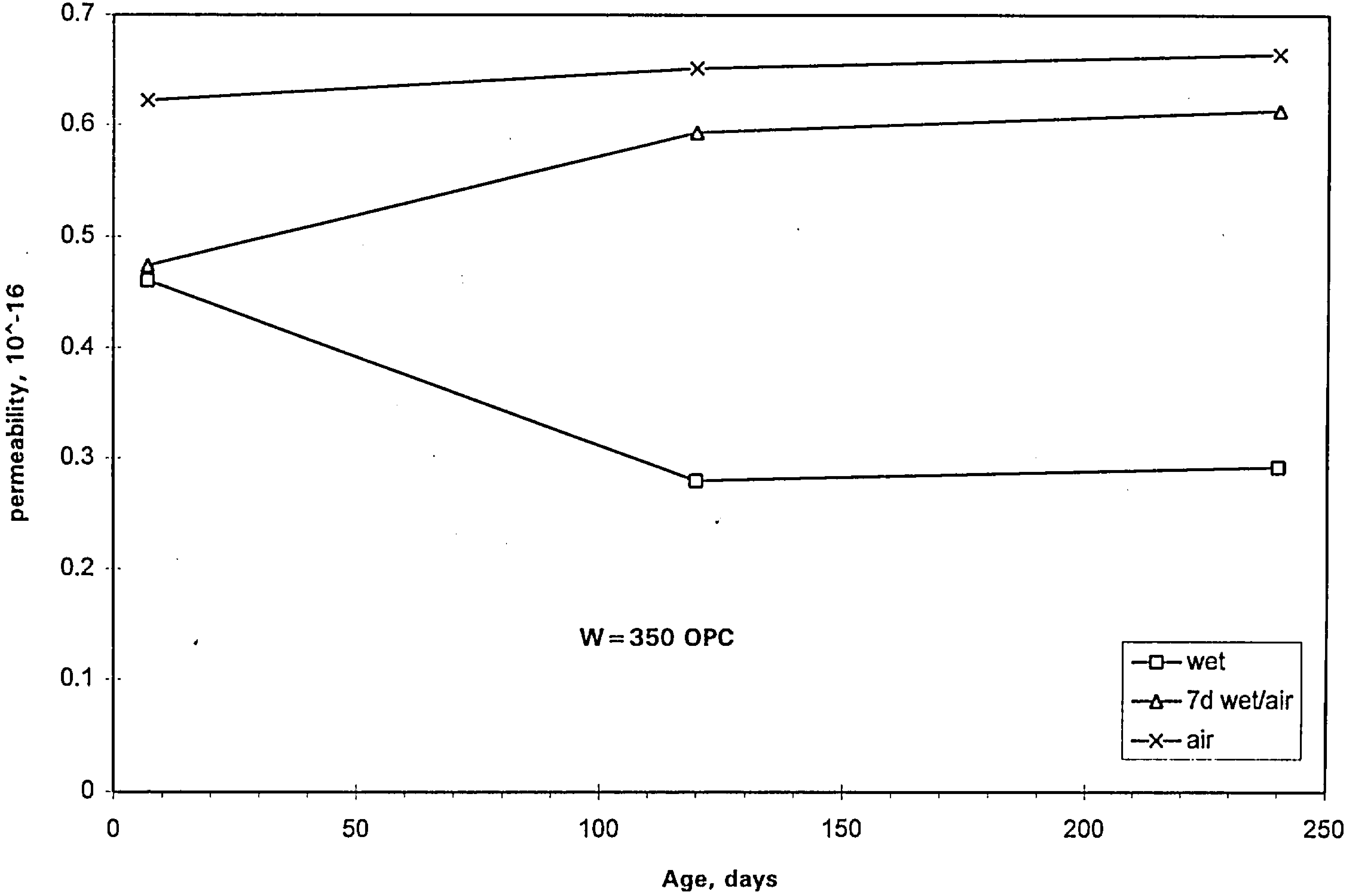


Figure 6.7 Influence of curing conditions on permeability of mix W

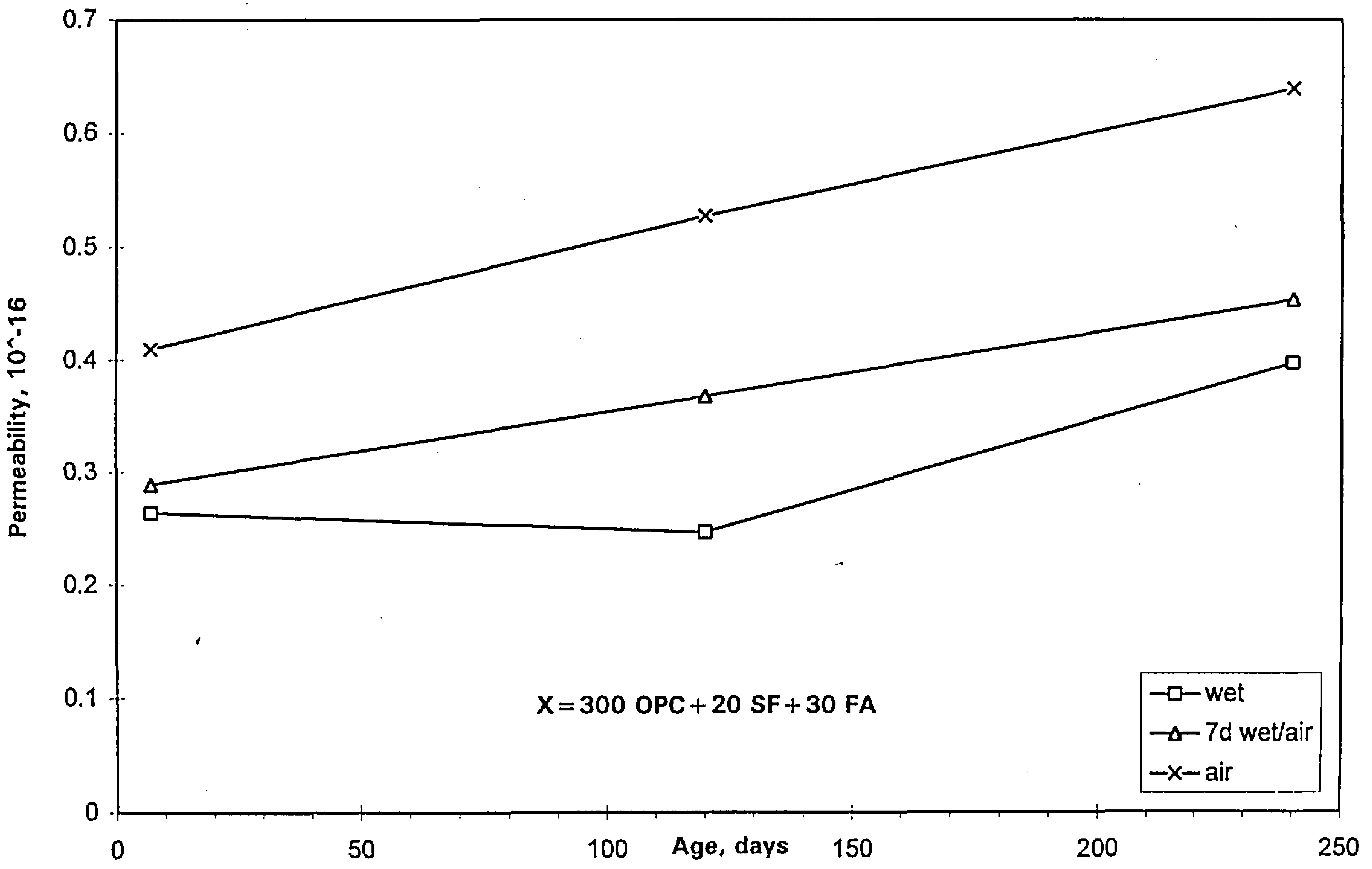


Figure 6.8 Influence of curing conditions on permeability of mix X

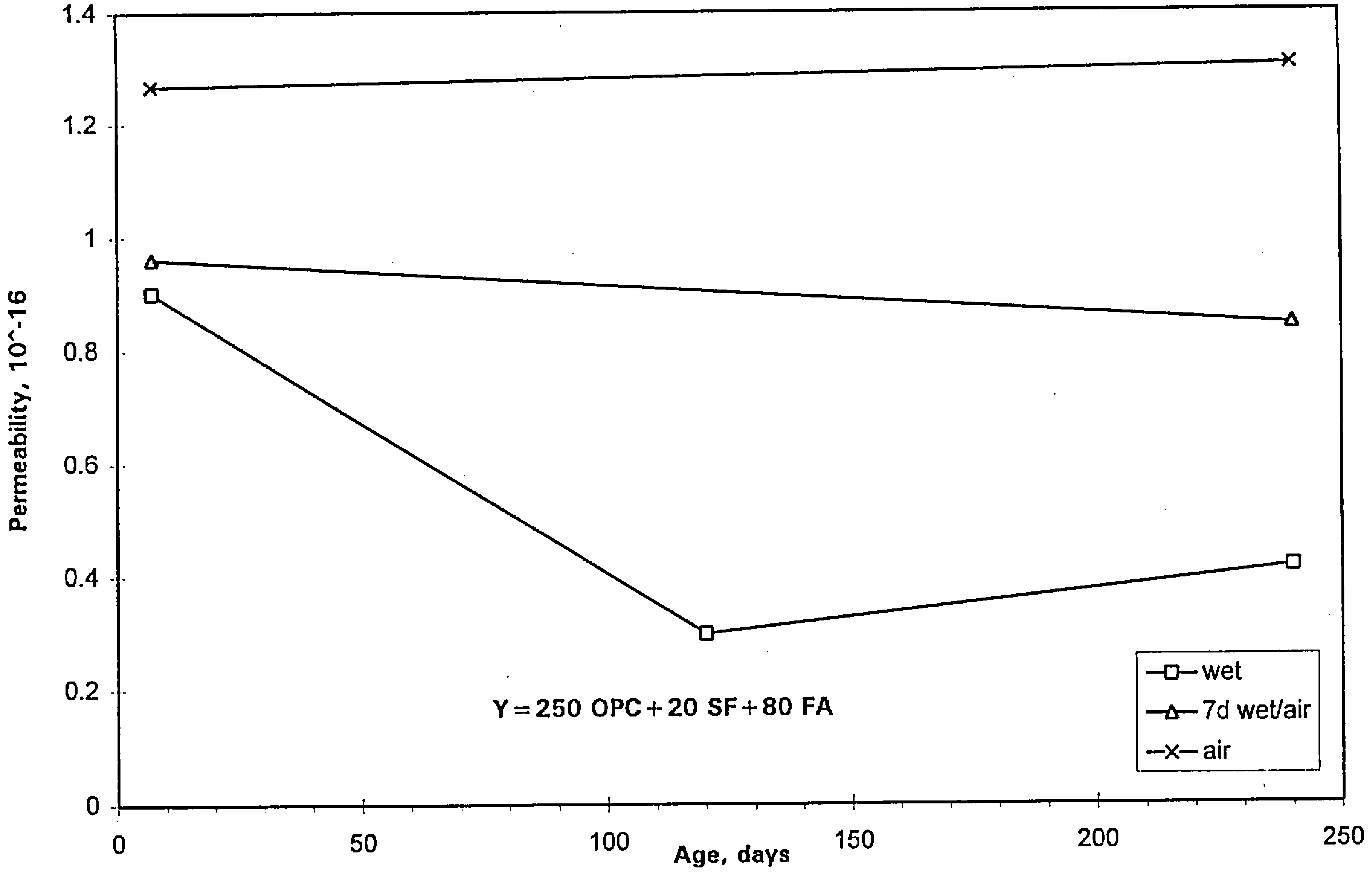


Figure 6.9 Influence of curing conditions on permeability of mix Y

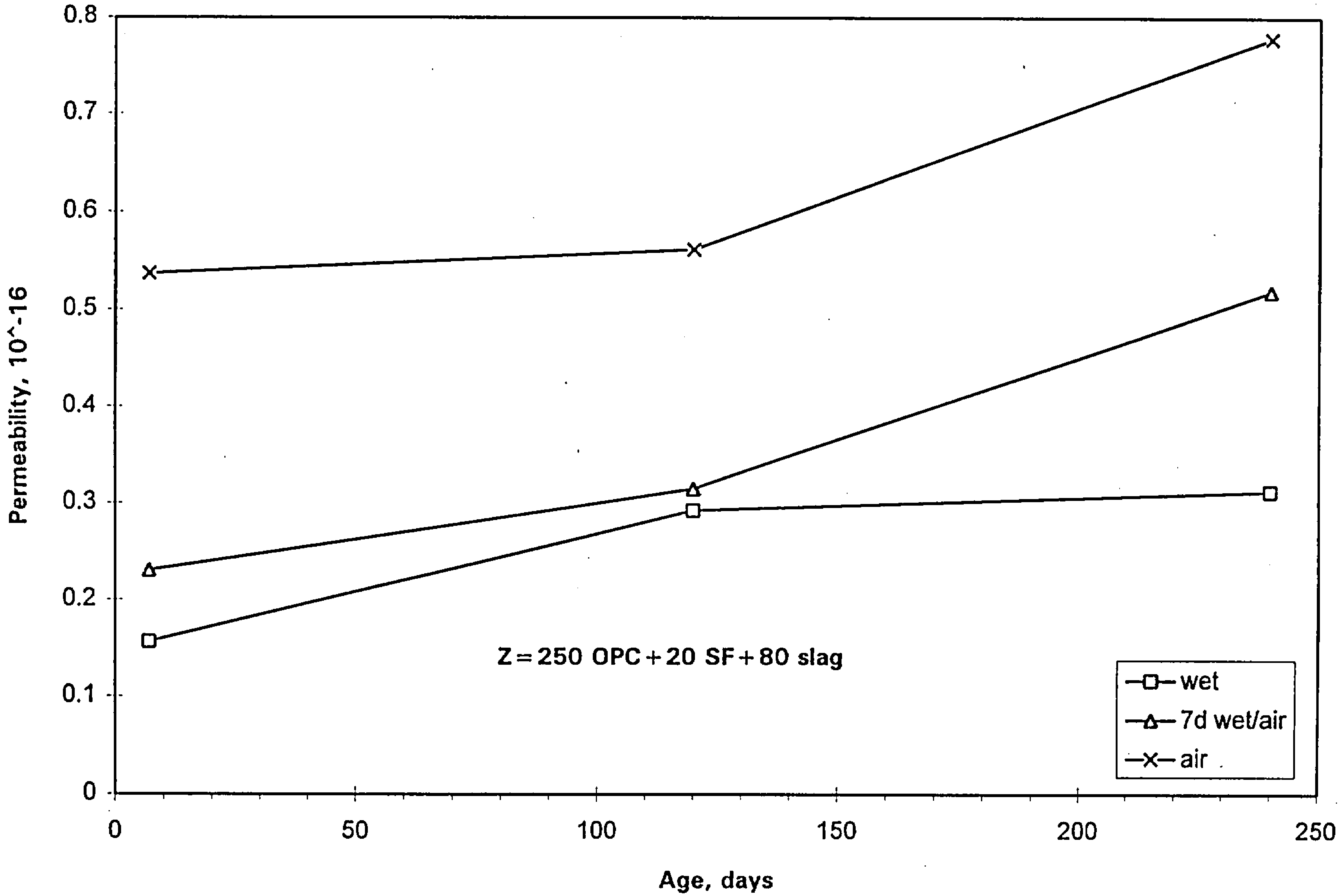


Figure 6.10 Influence of curing conditions on permeability of Mix Z

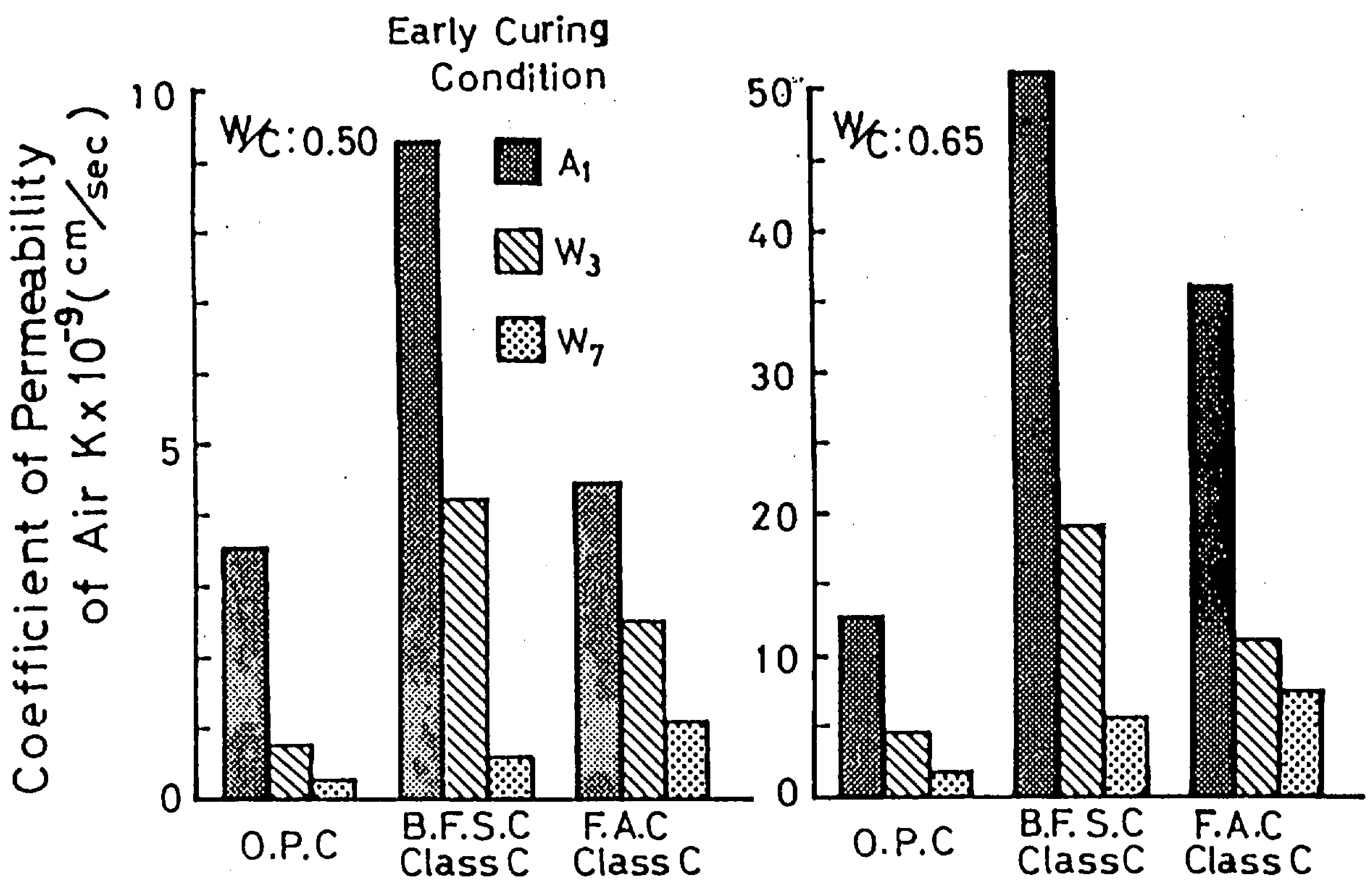


Figure 6.11 Relationship between early curing condition and coefficient of permeability if air at six months(pressure differens:2*10^5 Pa)[*69*]

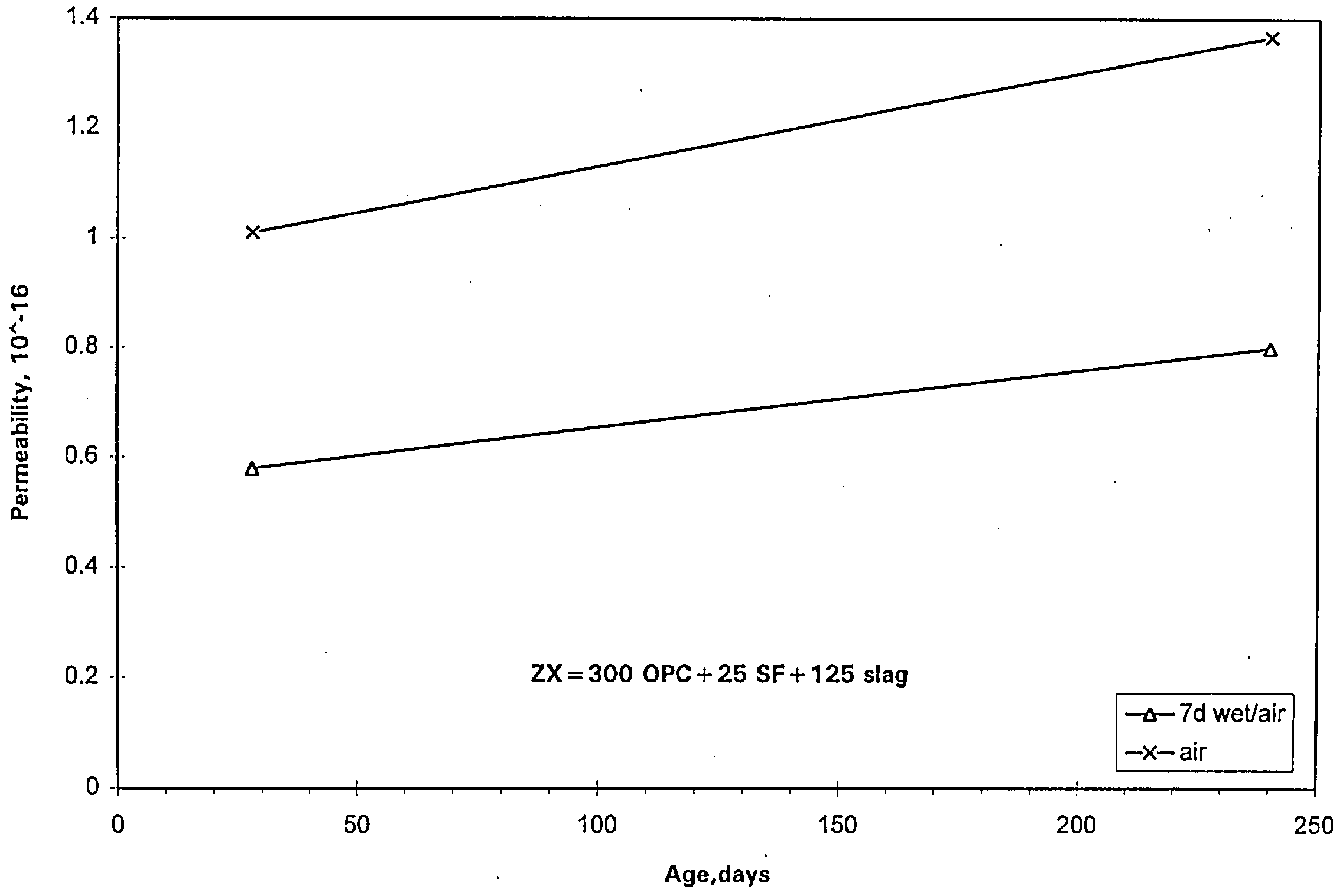


Figure 6.12 Influence of curing conditions on permeability of mix ZX

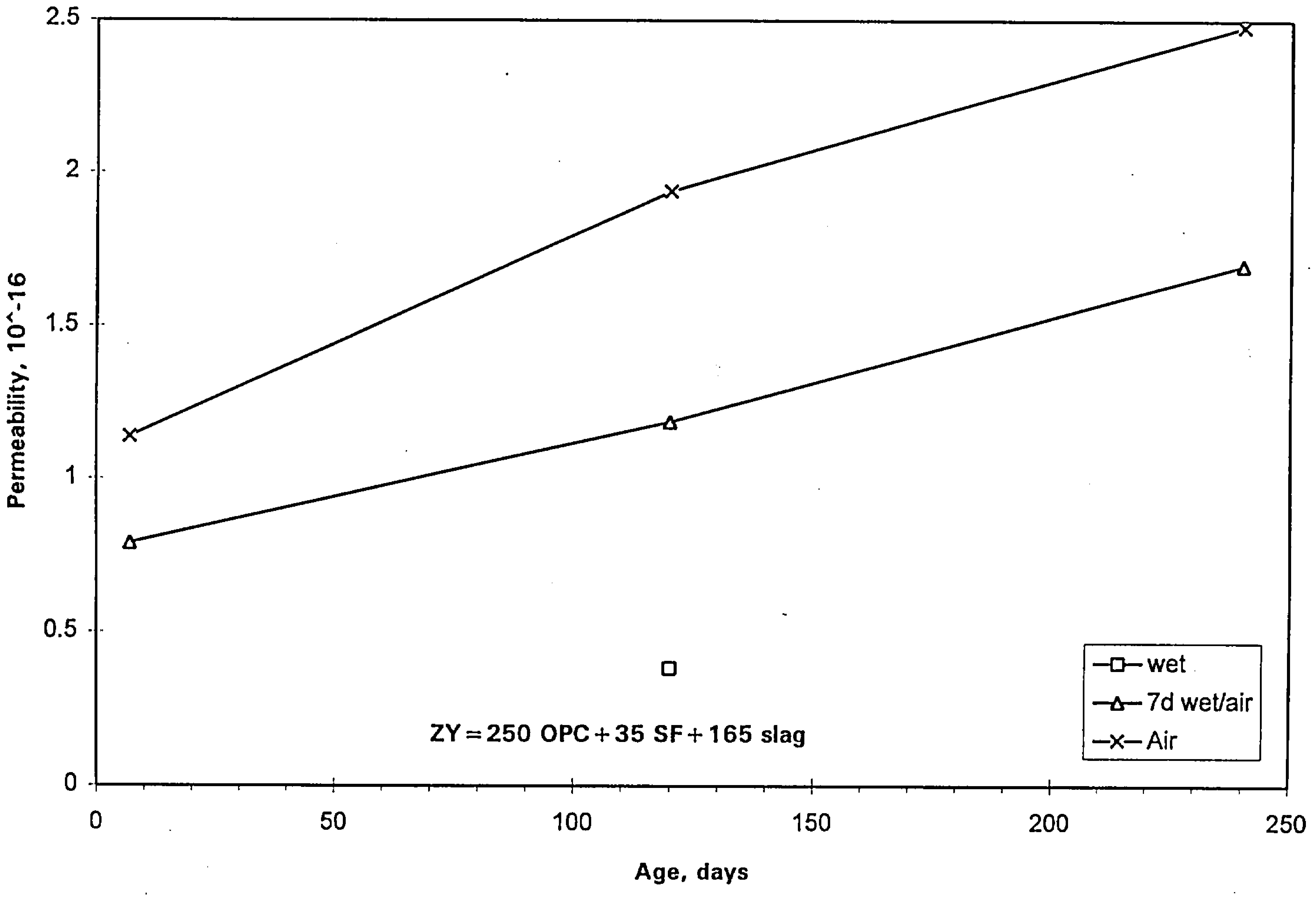


Figure 6.13 Influence of curing conditions on permeability of mix ZY

days. At of 240 days, the permeability of mix Y was slightly higher than that of mix X for which permeability was about 35% higher than the control mix permeability. Nagataki and Ujike [129] reported that the value of co-efficient of air permeability of concrete with the replacement ratio of FA below 20% is almost the same as that of concrete without FA. However, when the replacement ratio of FA is more than 30%, the coefficient of air permeability of concrete with FA is larger than that of concrete without FA. The increase of the coefficient of air permeability of concrete with FA cured in water for the period of 28 days was due to the increase of real water-cement ratio. The real water-cement ratio increases with the increase of replacement ratio of fly ash, as unit water content of concrete is kept constant.

Hughes [138] showed that extended periods of curing did not obtain lower OPC/FA paste permeability when compared to that of OPC. At 7 days the OPC/FA mix permeability was very high compared to that of the control, at 12 weeks it was still about 35% higher. The mix he used was 30% FA by weight of the cement and had a water/solid ratio of 0.47.

However, the values of permeability obtained under this investigation are much lower than those obtained by many other researchers, where they used FA as a replacement material.

In Figures 6.14-6.16 and 6.18 permeability of FA/SF and control concretes are compared under 7d wet/air-curing condition. It can be seen that, when 30kg/m^3 FA (mix X) was used, the permeability was improved at all ages compared with permeability of control mix. When the FA content was increased to 80kg/m^3 (mix Y) the permeability was twofold that of the control mix permeability. It could be said that permeability could be improved if the replacement level is kept below 80kg/m^3 (i.e. 25%).

Results of permeability of FA/SF mixes at different ages under air-curing condition are shown in Figures 6.14-6.16 and Figure 6.19. A similar trend to that of Figure 6.18 was obtained. Mix X permeabilities were slightly lower than those of the control mix, whereas mix Y exhibited larger permeability values compared with those of the control. This was expected because of prolonged drying and higher FA content. The results obtained are in agreement with results of Kasai et al [69], where it was found that FA concrete specimens which are not cured in water (i.e. air-curing) had a greater coefficient of air permeability than OPC concrete; the increase in permeability with age was also observed. FA concrete specimens cured in water until the age of seven days exhibited a higher coefficient of air permeability, increasing with time. It was concluded that the air permeability of blended cements is greater than that of Portland cements, the higher the content of FA in cement the greater the coefficient of permeability is, and that the permeability increases with age because the specimen is dried more.

Lynsdale [93] found that mix containing 30% FA and with water/solid ratio of 0.4 exhibited a marked increase in permeability when compared to that of the control and showed no reduction with age after age of 3 days. He suggested that coarsening of pore structure produced by FA which was detected by MP might be a reason. He concluded that the system is not fully understood and requires further investigation and the real cause, however, may be explained by studying the air content system of the mixes.

6.4.2 Oxygen permeability of concrete mixed with slag/SF

Figures 6.14-6.16 and Figure 6.20 show the oxygen permeability of slag/SF concrete mixes. Under continuous water-curing the permeability of the 80 kg/m^3 slag (mix Z) is much lower than the control mix permeability. At 120 and 240 days age the permeability of this mix was the same as that of control mix and was in the range of 0.30m^2. By increasing the cement replacement level, 165kg/m^3 slag and 35kg/m^3 SF (mix ZY) the oxygen permeability was slightly increased compared to the corresponding control mix permeability. This means that the incorporation of slag plus SF could bring improvement in permeability provided sufficient water-curing is provided, and that 40% of slag replacement level might be a good figure as a guide for replacement level. Compressive strength, pulse velocity and dynamic modulus results as well as pore structure measurements are in good agreement with this conclusion. When early curing in water is carried out for longer periods for this type of slag/SF concrete (ZY mix) the co-efficient of permeability would become lower, because the cement paste of mortar is hydrated to a greater degree and is more compact. If the specimens were not cured well, as can be seen from the data in Table 6.1, the matrix would have been coarser and this results in larger coefficient values. However, because of the complex nature the microstructure in hardened cement blended concrete , it is desirable to use more than one experimental method to measure permeability.

Figure 6.21 shows the permeability of control and slag/SF concrete mixes under 7d wet/air-curing condition. Mix Z of 80kg/m^3 slag and 20kg/m^3 SF displayed the lowest oxygen permeability co-efficients, followed by the control mix (W), mix ZX of 125kg/m^3 slag and 25kg/m^3 SF, and mix ZY, at all ages of curing. In the case of 7d wet/air-curing, the value of coefficient of oxygen permeability with the replacement level of slag 80 kg/m^3 is lower than that of the control concrete without replacement materials.

However, when the replacement level of slag is more than 125kg/m^3, the co-efficient of oxygen permeability of concrete with slag is larger than that without slag. This result indicates the importance of curing to achieve slag/SF concrete of low permeability and hence good durability, especially if the replacement level is high. It also indicates that high early strength of Z concrete has the smallest coefficient of oxygen permeability.

Figure 6.22 shows the effects of replacement of slag/SF on oxygen permeability of air cured specimens. The figure shows a similar trend to that of Figure 6.21 The results obtained show an explicit increase in the oxygen permeability of mix ZY which incorporated 165 and 35 kg/m^3 of slag and SF respectively, compared with mixes W, Z and ZX. The co-efficient of permeability increases more under air-curing condition with the increase in slag/SF regardless of the curing age. These results are in agreement with pore structure measurements and mechanical properties such as strength, pulse velocity, dynamic modulus and shrinkage obtained under air-curing condition. This poor performance in oxygen permeability could be explained, by the fact that slag/SF, like other pozzolanic materials, has pozzolanic activity and needs water for hydration to develop their properties. Hydration product, in air-curing condition, is not sufficient and does not block the pores of slag/SF concrete and hence no improvement against the permeability of gases is expected. And slag/SF under no curing, regardless of percentage of replacement, would make the internal structure of concrete coarser, in spite of increased compressive strength.

In general, from the relationship between the early curing condition and the coefficient of oxygen permeability of OPC, FA/SF and slag/SF concretes at different ages, it could be said that when the early curing in water is carried out for larger periods the coefficient of permeability becomes lower, because the cement paste of mortar in concrete is hydrated to a greater degree and is more compact or dense. If the specimen is not cured well, the pore structure is coarser, and this results in larger coefficient values.

6.5 Relationship between permeability and compressive strength

The compressive strength of concrete is, in most specification, the dominant parameter used to "control" the quality of concrete [2]. However, in recent years, with the developments in concrete technology it is accepted that the performance of concrete under a particular environment cannot be solely related to its strength but that it is a function of its pore structure and permeability [86,139].

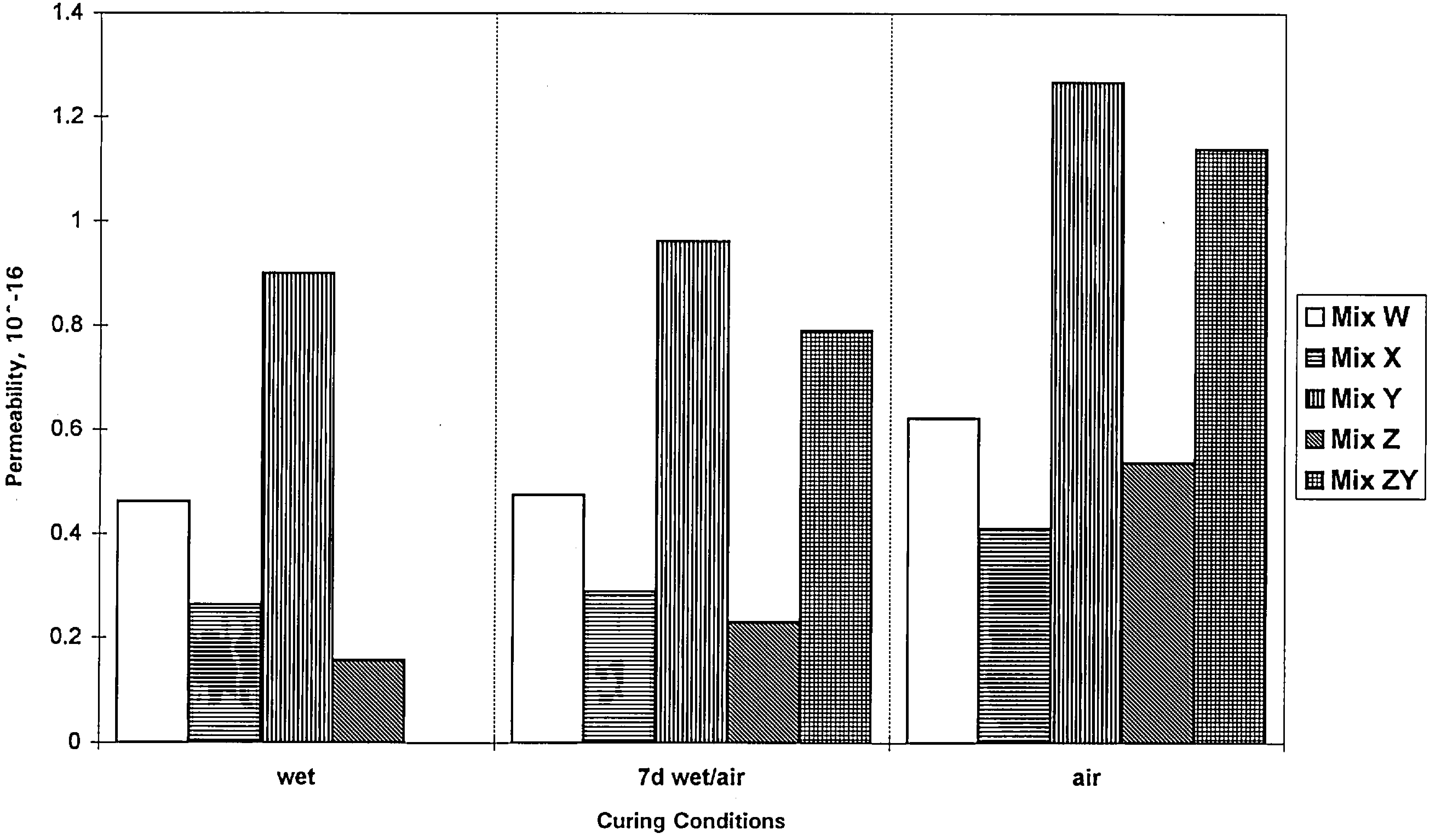


Figure 6.14 7-day permeability for various blended cement mixes

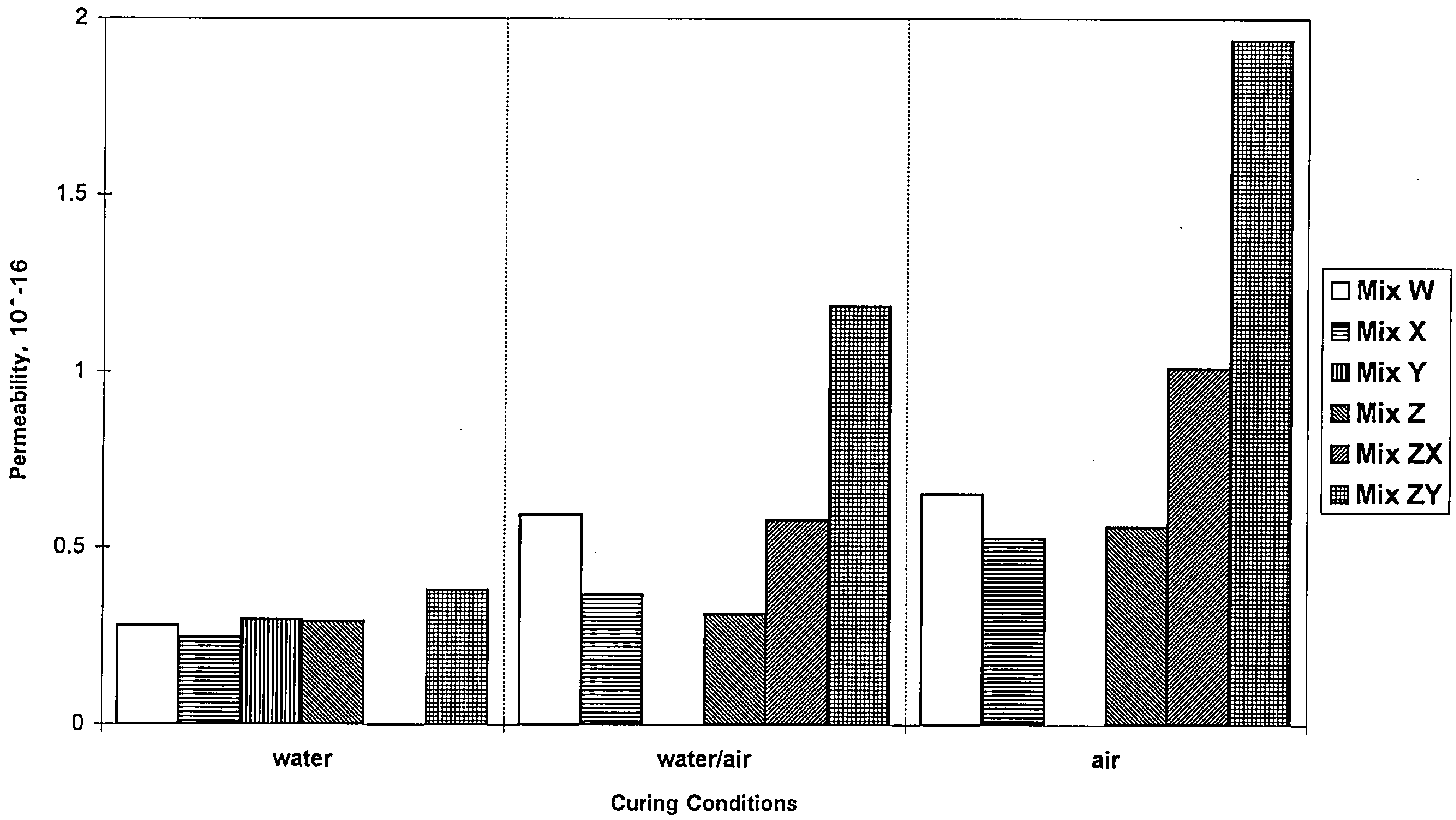


Figure 6.15 120-day permeability for various blended cement mixes

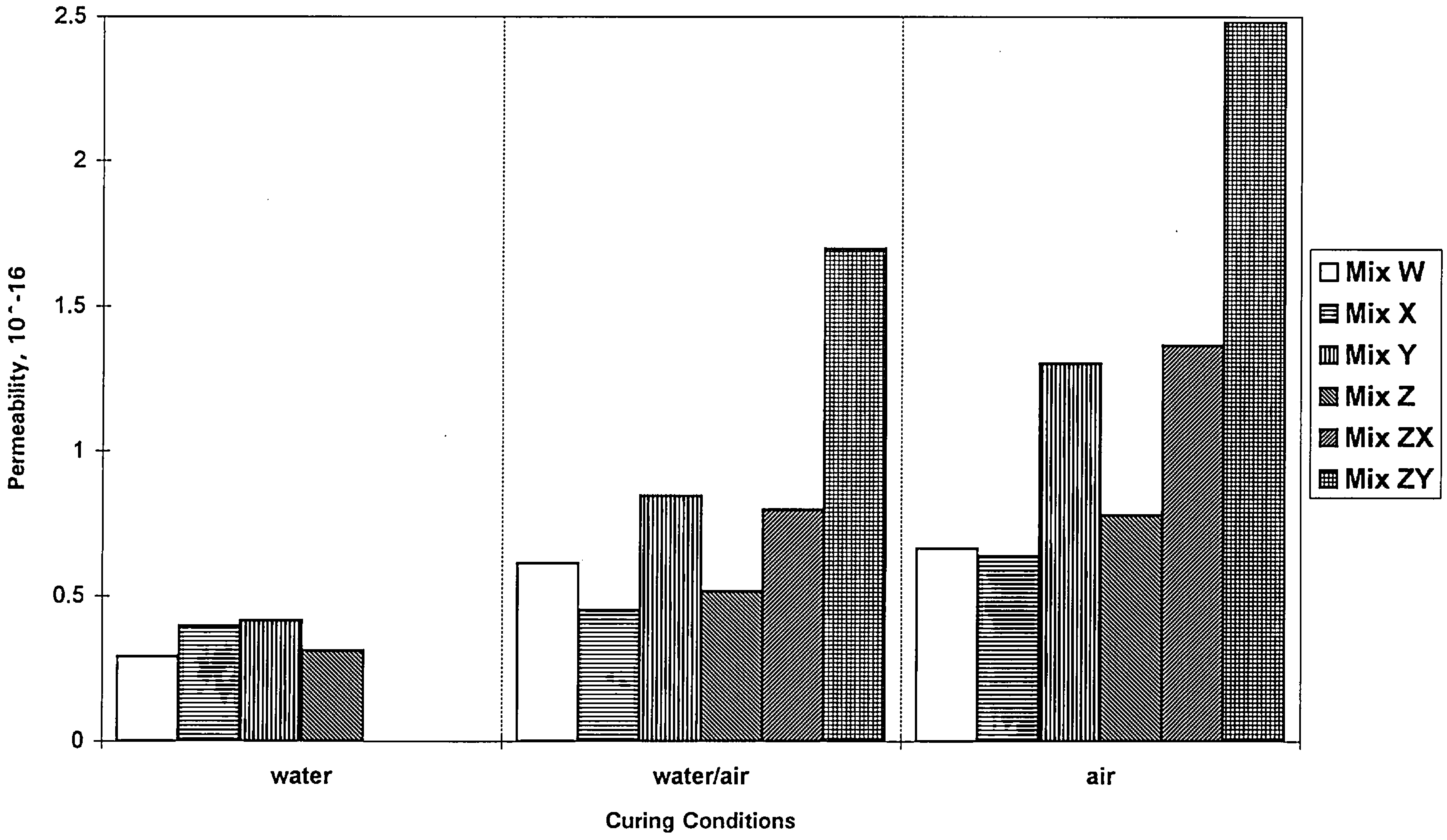


Figure 6.16 240-day permeability for various blended cement mixes

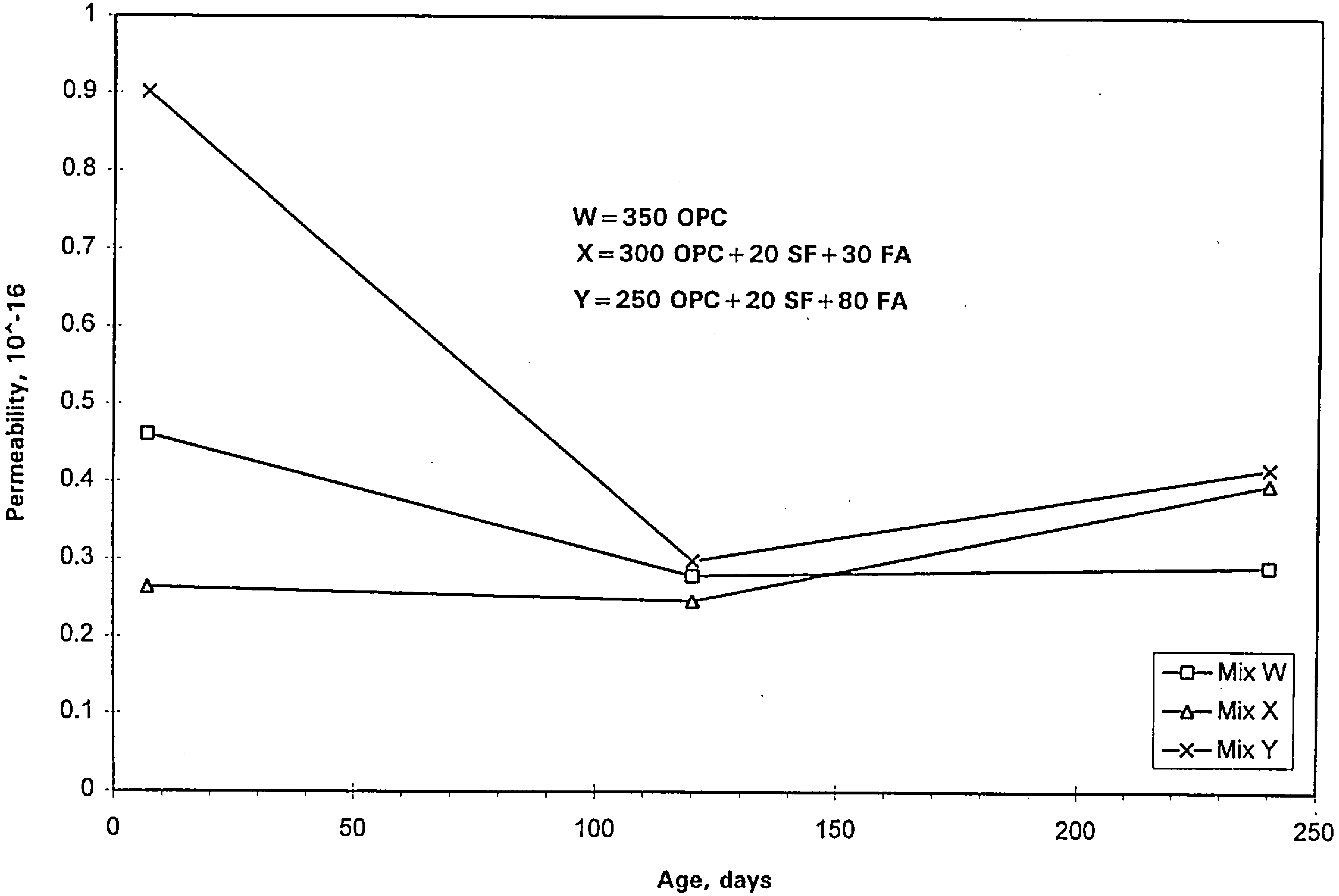


Figure 6.17 Effect of FA/SF on permeability of wet-cured specimens

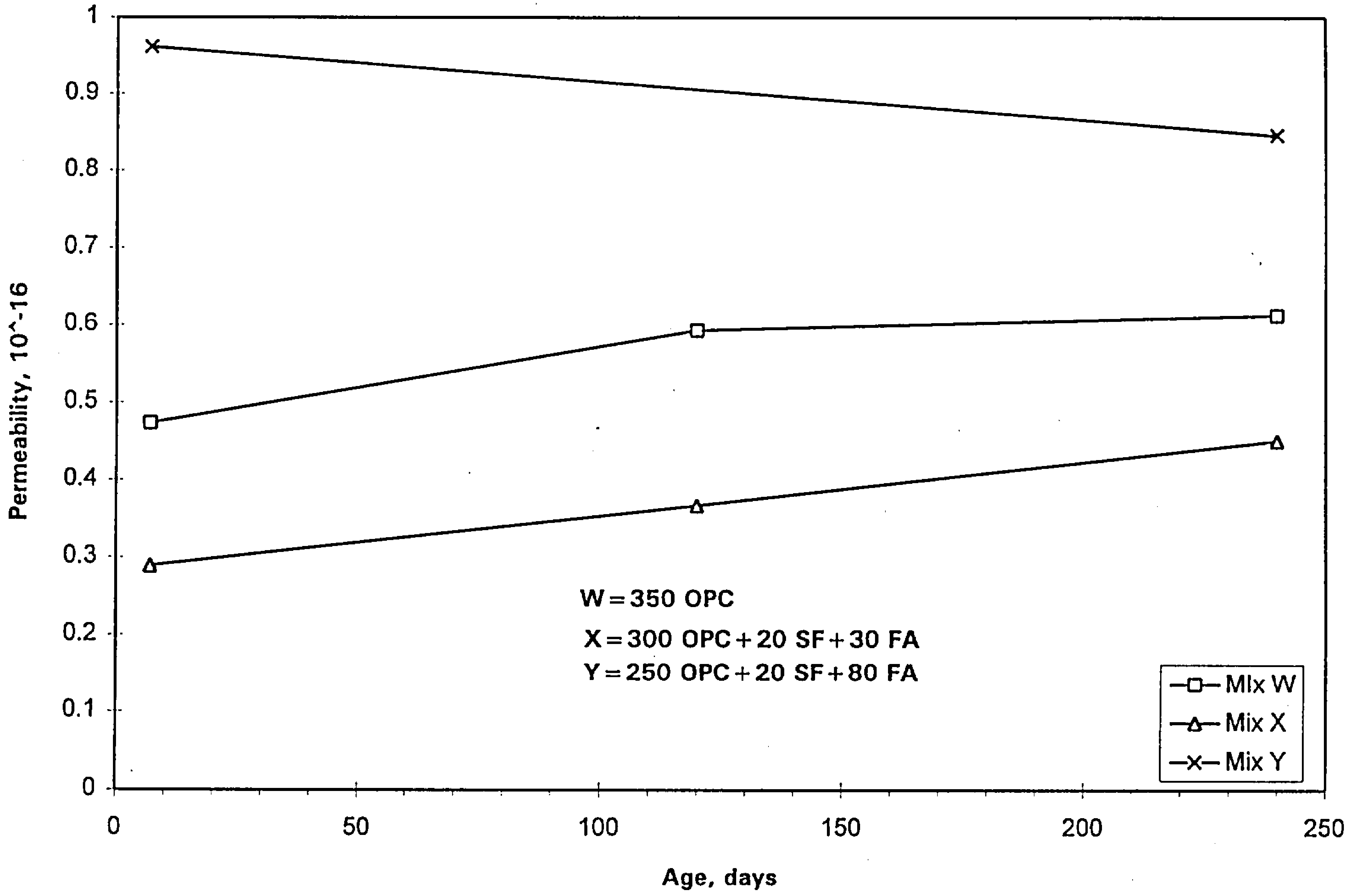


Figure 6.18 Effect of FA/SF on permeability of 7d wet/air- cured specimens

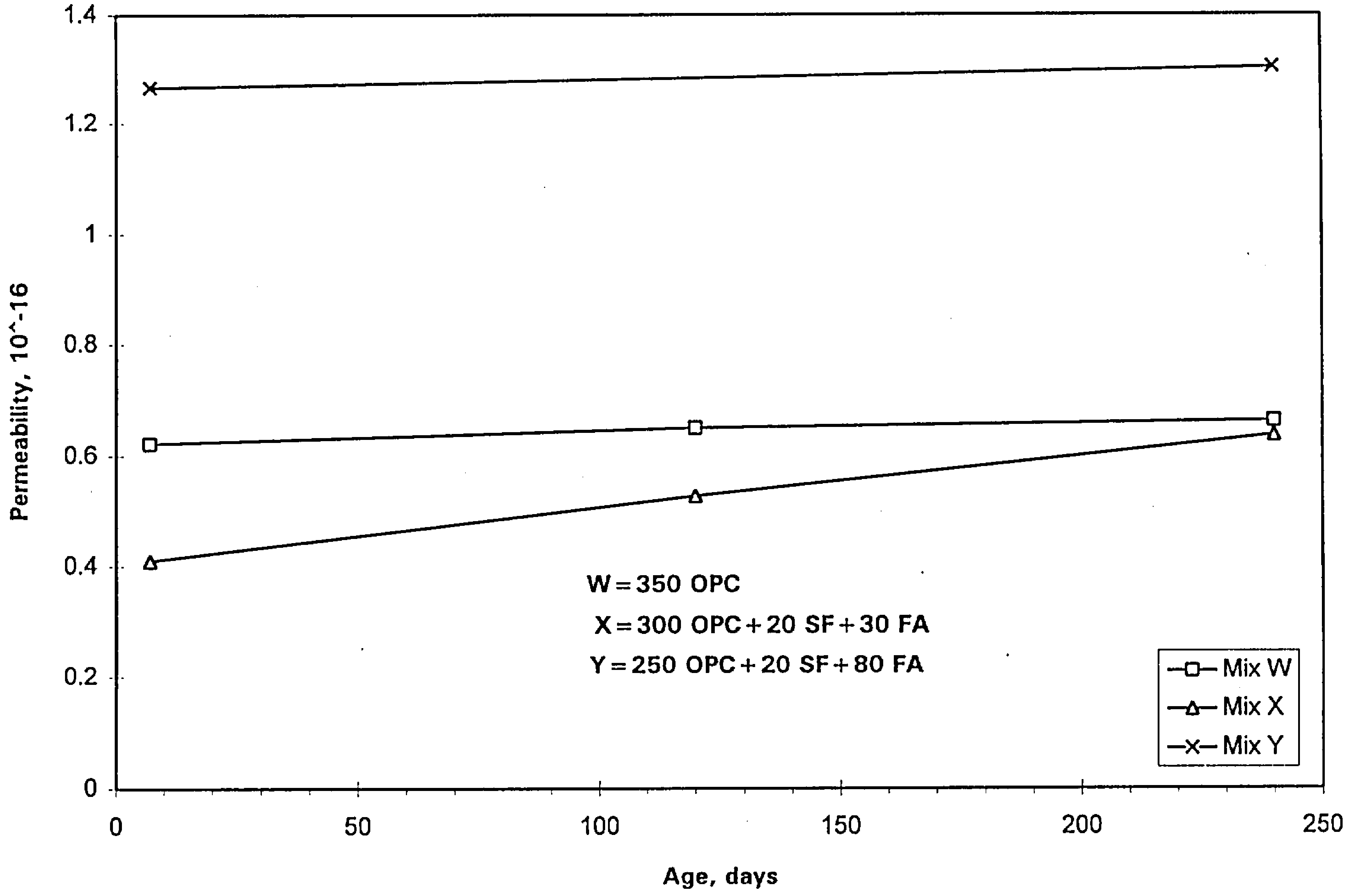


Figure 6.19 Effect of FA/SF on permeability of air-cured specimens

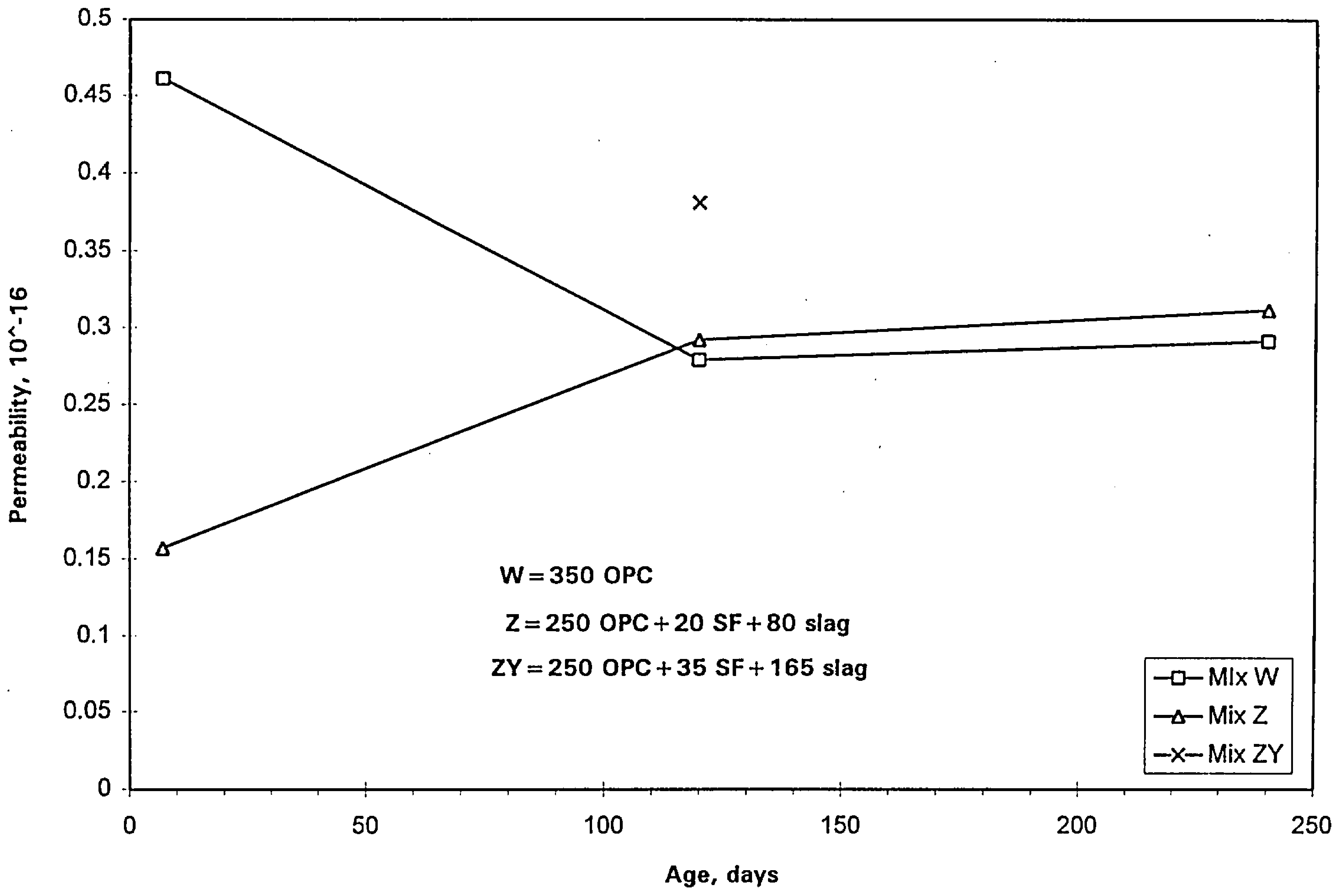


Figure 6.20 Effect of slag/SF on permeability of wet-cured specimencs

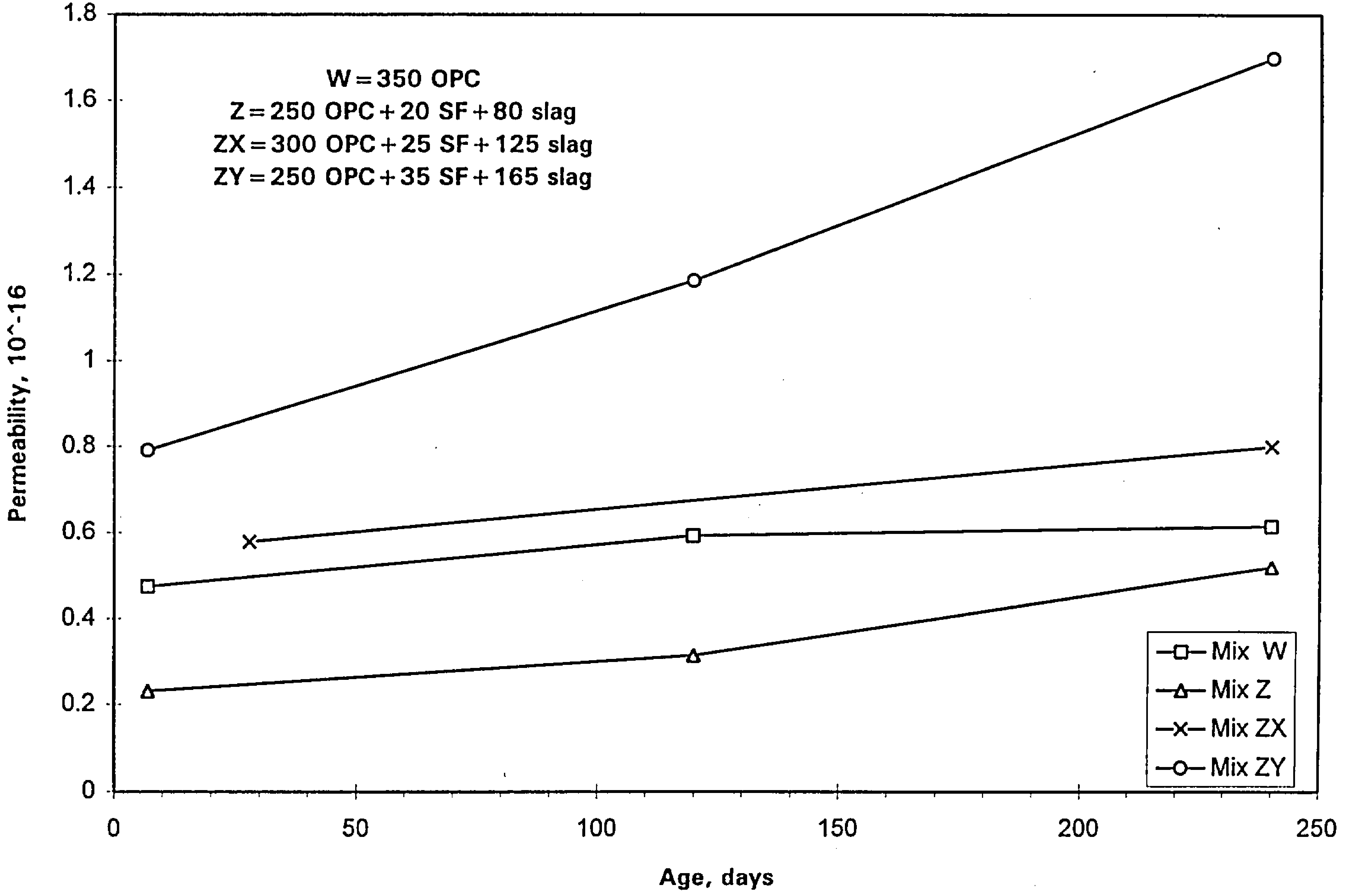


Figure 6.21 Effect of slag/SF on permeability of 7d wet/air cured specimens

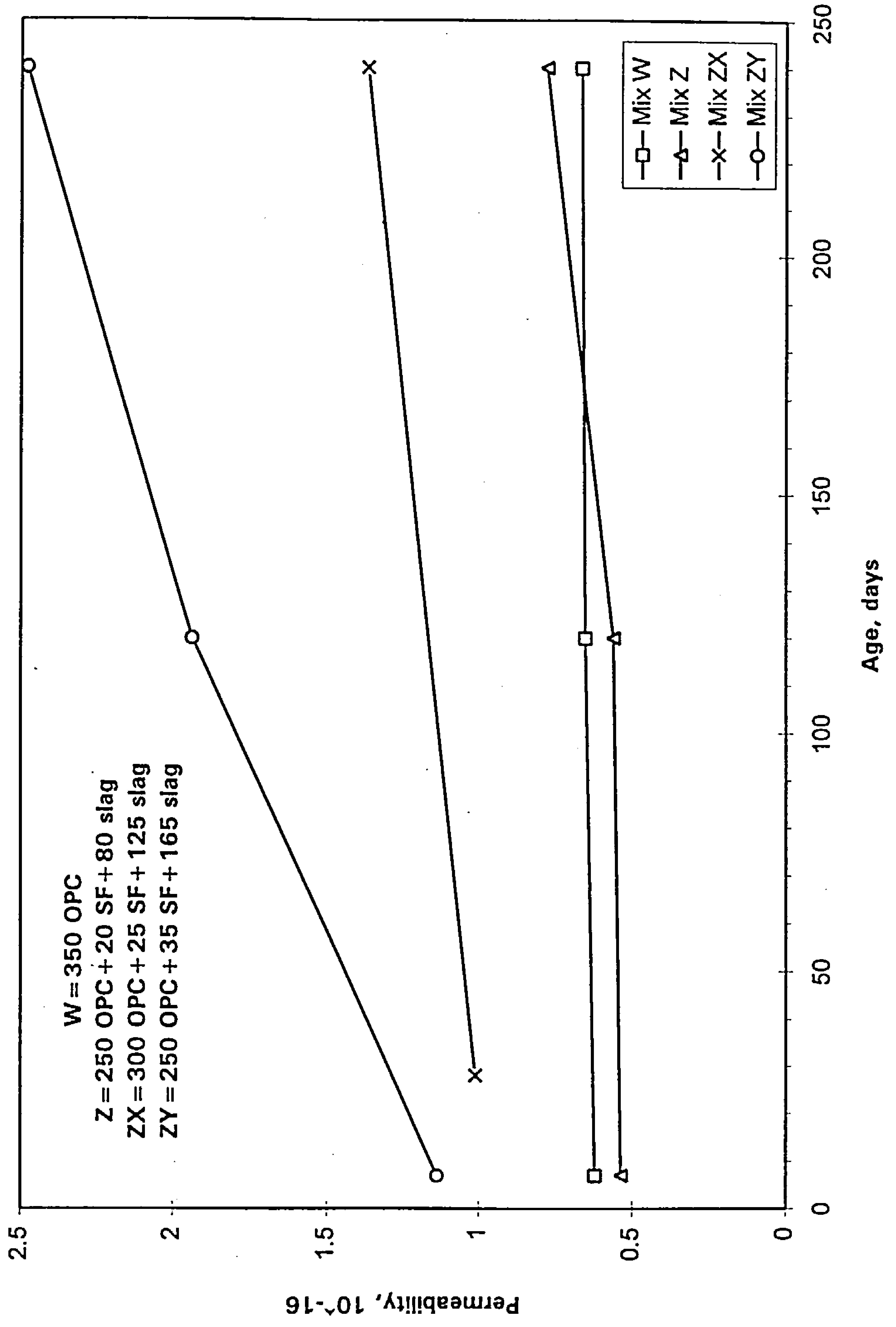


Figure 6.22 Effect of slag/SF on permeability of air-cured specimens

The results obtained in this investigation indicate that permeability is a function of compressive strength and pore size distribution, and that compressive strength on its own is not enough to assess the performance and durability of concrete. Figure 6.23 shows the relationship between oxygen permeability and compressive strength for different concrete mixes cured at 20°±2°C under continuous wet, 7d wet/air and air-curing conditions. The results plotted in this figure indicate that permeability reduces as strength increases, however they are scattered such that concretes of similar compressive strengths can exhibit a wide range of permeabilities, depending on pore structure of concretes where: (1) the composition is varied either by changing the cement replacement level or by changing the cement replacement materials (FA/SF or slag/SF) and (2) varying the curing regimes whether wet, 7d wet or dry.

Results reported by Cabrera et al [2] for concrete mixes made with OPC and OPC/FA cured in a fog room at 20°C and 100% relative humidity show similar trends between permeability and compressive strength, i.e. permeability reduces as strength increases. They [2] said that although there is a good relation between permeability and strength for a particular concrete, the relation cannot be generalised for concretes where the composition is varied either by changing the aggregate-cement ratio or by changing the type of cement by adding chemical additives. The results of their investigation confirm the fact that permeability is related to compressive strength for any one mix but when a relationship is attempted for all mixes the result is a cloud diagram as shown in Figure 6.24.

Also, results reported by Lawrence [71] for concrete mixes made with OPC, OPC/FA and OPC/slag cured in water at 20°C show about similar trends to those in Figure 6.23, i.e. the permeability-strength results fall within a wide band. However, he [71] concludes that to a: 'good approximation, there is a single relationship between strength and permeability for concretes containing either Portland cement or those with partial replacements of ground granulated blastfurnace slag or fly ash.'

From the above discussion, however, it can be suggested that there is no unique relationship between permeability and compressive strength which covers a wide range of mixes varying in their microstructural characteristics. In addition this relationship is also influenced by the type of curing. For about the same compressive strength value air-cured concrete exhibits higher permeability than its wet and 7d wet/air-cured counterparts, indicating a coarser microstructure for the air-cured specimens.

6.6 Relationship between oxygen permeability and threshold diameter

Engineering properties of concrete such as strength, permeability and diffusivity (and thus durability) are known to be influenced by pore structure. The rate of movement of water through concrete has an important bearing upon the possible degree and rate of determination of reinforcing sheet or concrete itself in aggressive environments. Thus, from an engineering viewpoint there is a distinct advantage in being able to correlate pore size distribution to permeability. Many researchers attempted to correlate permeability to different parameters representing the pore size distribution of concrete [102,138,140,141]. For example Mehta and Manmohan [73] reported that a correlation is found between the permeability of cement paste and the volume of pores greater than 0.132 μm diameter. Others [102,140] successfully used the threshold diameter to correlate the pore structure of concrete to its permeability.

In this investigation, however, the best relationship was found between the oxygen permeability and the threshold diameter. The importance of threshold diameter for flow becomes obvious when one considers that a pore channel can only contribute significantly to flow when it is relatively large and connected all the way across the sample [140]. In fact studies of the pore size distributions of hardened cement paste [101,142,143], as well as this study, generally indicates the existence of threshold diameter, which is defined by Nayame and Illston [102] as "maximum continuous pore radius" which they use to characterise permeability.

The threshold diameter obtained from the mercury intrusion porosimetry and the oxygen permeability are plotted in Figure 6.25, and a linear relationship was found in the form:

$$y=-0.131+0.513x \qquad (6.4)$$

where: y = threshold diameter
x = oxygen permeability

From the figure it can be seen that for all mixes and curing conditions the permeability is reasonably correlated with threshold diameter, as threshold diameter increases the permeability increases. The reduction in threshold diameter and permeability accompanying hydration due to wet or 7d wet/air-curing is shown in Figure 6.25, which also indicates that there would be a reversal of this trend if drying is prolonged. It is noticeable that air-cured specimens exhibit similar patterns, so that permeability and the maximum continuous pore radius are apparently related under the adverse effects of air-curing. This means that larger pores are likely to offer the least resistance to water flow or aggressive agents to penetrate into concrete, and obviously the majority of the flow will occur in the volume represented by the threshold diameter, i.e. by the maximum continuous pores. In fact, only one large passage connecting capillary pores will result in a large permeability, while the porosity could remain virtually unchanged [3]. From the durability viewpoint, it may be important to achieve low permeability and have low pores of continuous diameters. Therefore, the wet and 7d wet/air-cured specimens threshold diameter is advantageous because the considerable proportion of small pores carry very little of permeating water or allow aggressive agents.

Winslow and Diamond [101] visualised the penetration of mercury at threshold diameter to be analogous to flow through the main continuous channels of a river system whilst the penetration at the rest of the pores correspond to flow through local side channels.

Mehta [73] reported that in general with increasing age of curing (the degree of hydration) there was a reduction in the threshold diameter, and the cumulative volume of pores at any given diameter. The results obtained in this investigation seem to confirm these findings.

6.7 Conclusions

In this chapter, the oxygen permeability of concrete mixes made with and without cement replacement materials is reported. Due to the complexity of the system investigated and many factors that affect permeability of concrete, it is difficult to pinpoint one parameter which can readily explain the variability of the permeability results. The main results obtained are as follows:

It was found that the main technique is capable of measuring permeability of concrete mixes and producing satisfactory results. However, when using this technique to assess the effect of aging for wet-cured specimens, it was found that the results were somewhat contradictory to the expected trend that the permeability decreases with age. This suggests that for examining the influence of aging on permeability for wet-cured mineral admixtures concretes another technique might be preferable, viz. water permeability technique.

1. The specimens cured continuously in water exhibited the lowest oxygen permeabilities at all curing ages compared with 7d wet/air- and air-cured specimens.

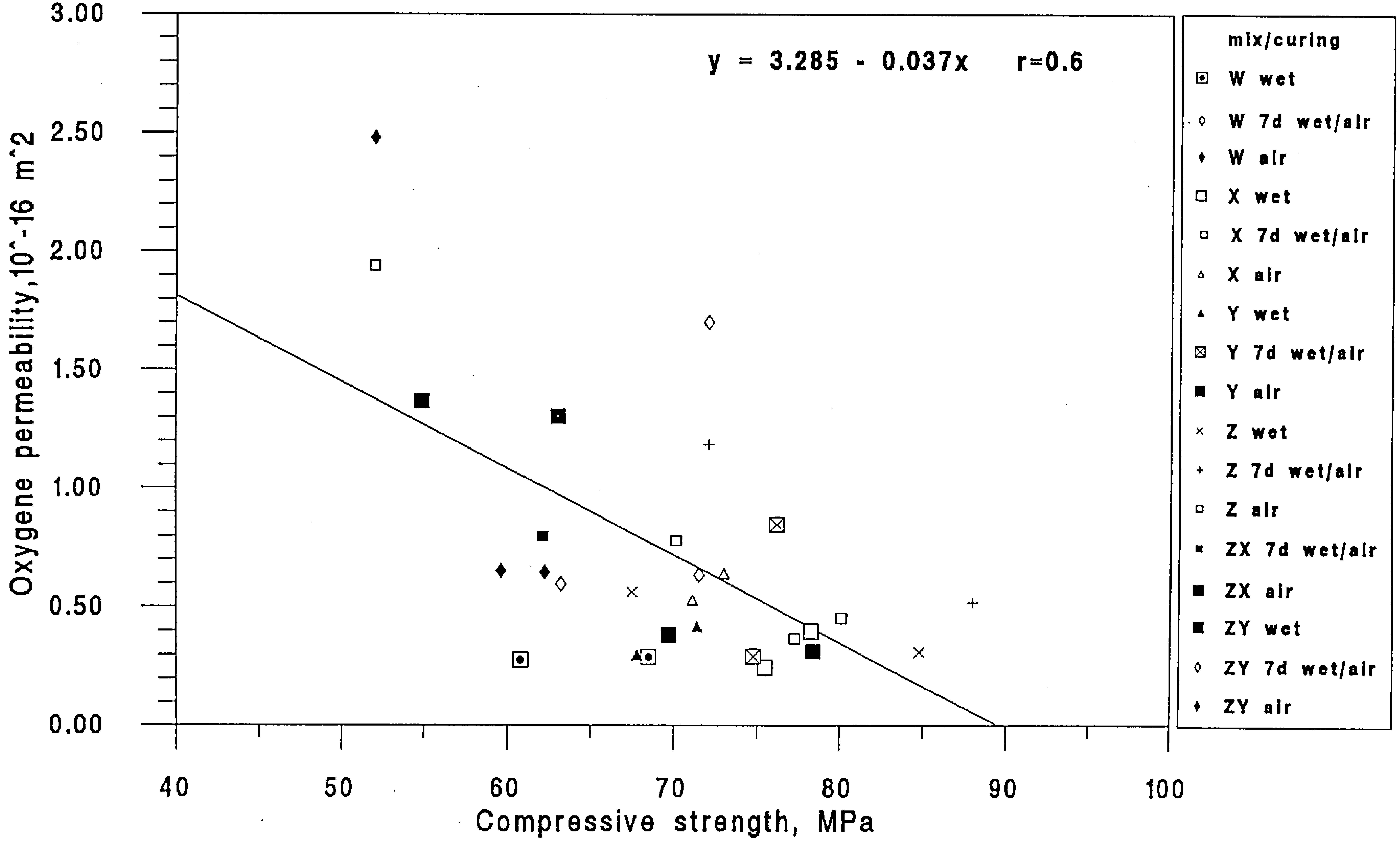


Figure 6.23 Relation between compressive stringth and permeability

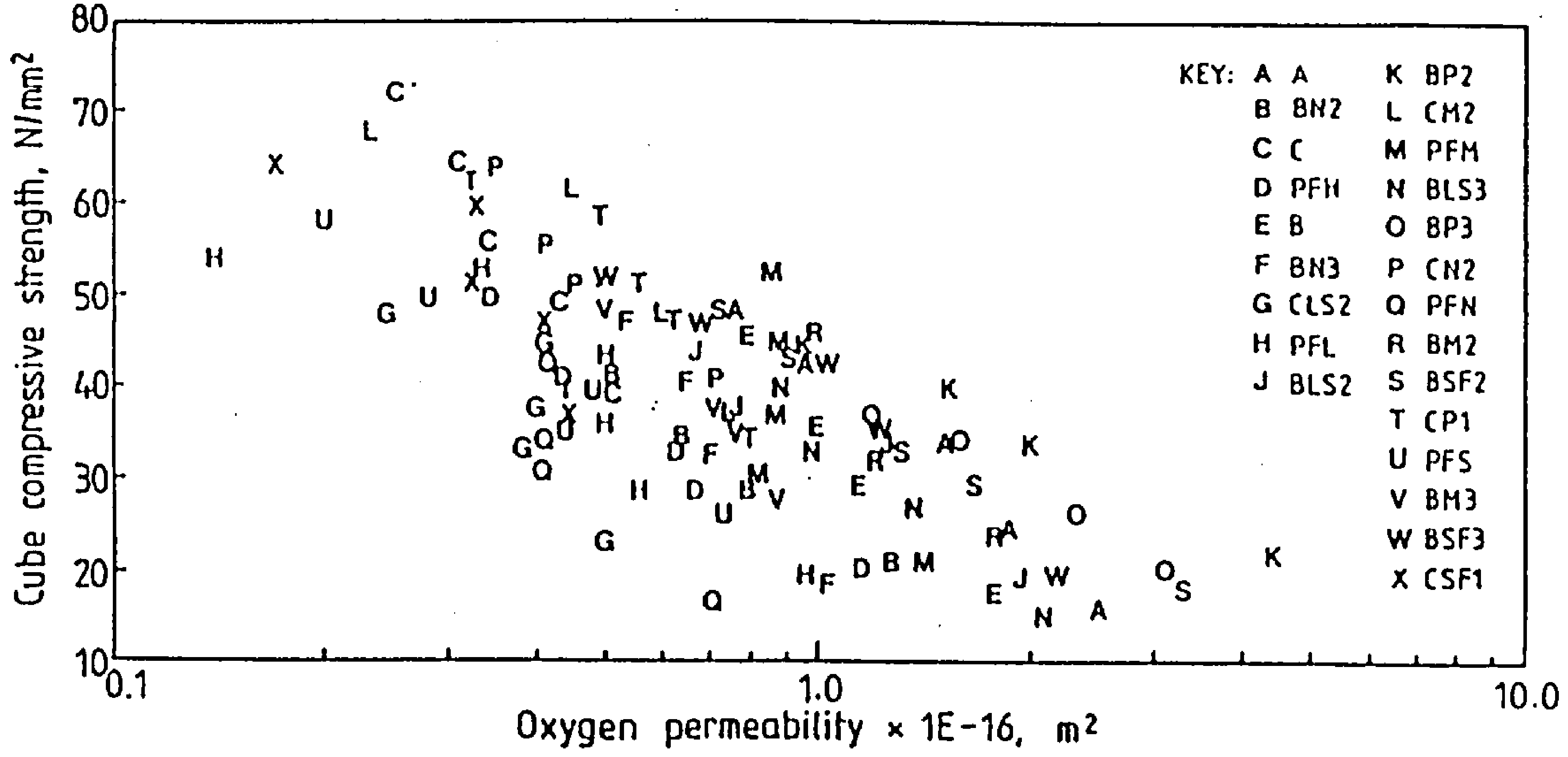


Figure 6.24 Cloud diagram relating compressive strength to permeability [2]

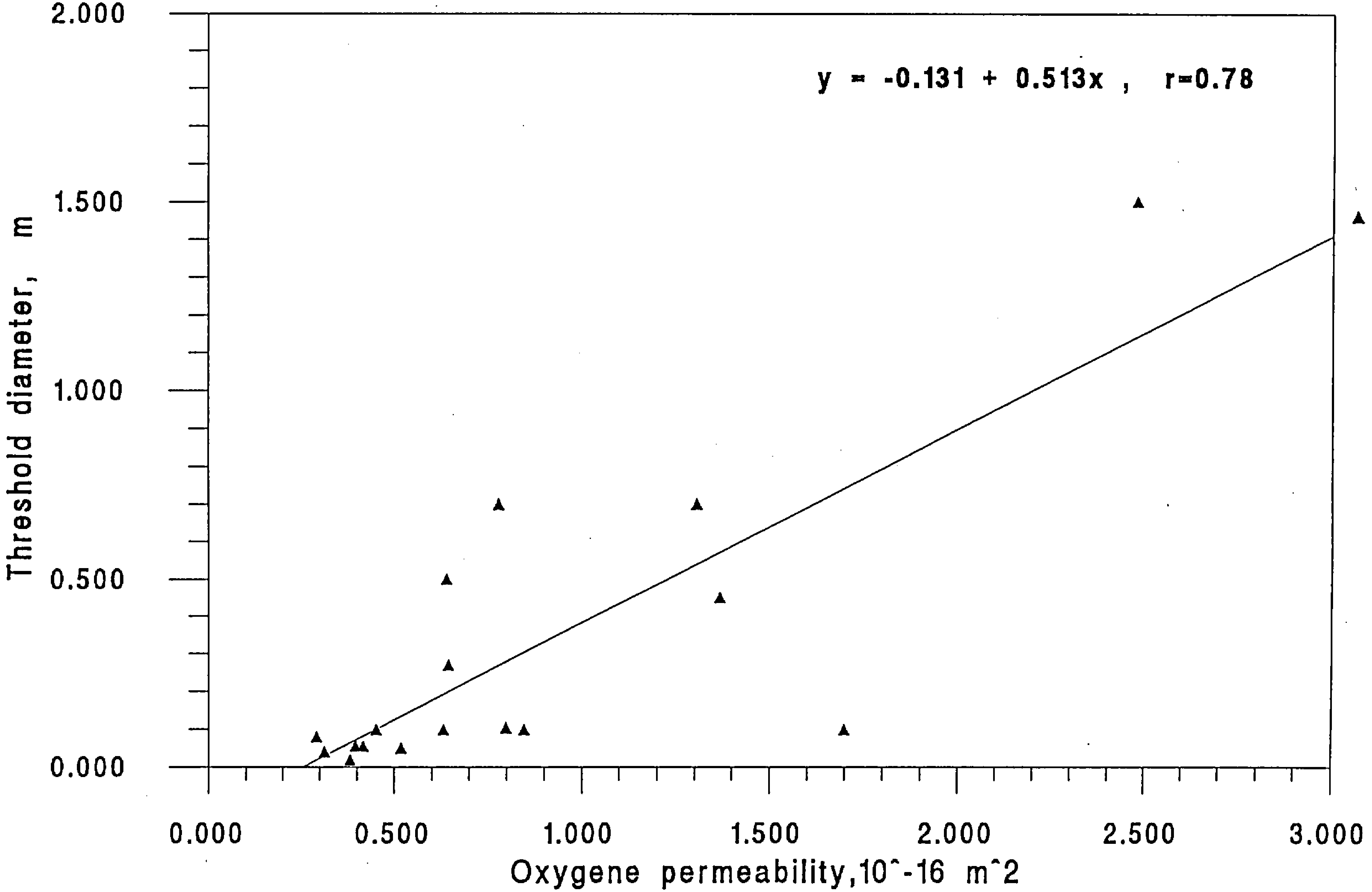


Figure 6.25 Relation between permeability and threshold diameter

2. The permeability of air-cured specimens is greater than 7d wet/air-cured specimens. When the early moist curing was carried out for 7 days the permeability becomes lower, because the cement paste of mortar is hydrated more resulting in a compact matrix, whereas in air-curing, the limited hydration is not of a magnitude that allows the generation of enough hydration product for the narrowing and blockage of passages of pores within the interconnected pore network.

3. Complete drying (conditioning specimens at 105°C) seems to be responsible for the increase of the coefficient of oxygen permeability of concretes with age as a result of shrinkage cracking which modifies the pore structure, leading to artificially high permeability values. Thermal shock due to immediate transfer of samples from 20°C to 105°C might also lead to internal microcracing.

4. 165kg/m^3 slag and 80 kg/m^3 FA blended mixes are very sensitive to prolonged drying, their permeability is much more influenced by no early moist curing than that of other concrete mixes.

5. Concretes containing 30 kg/m^3 FA and 80 kg/m^3 slag showed lower permeability compared to equal grade OPC concretes, under the three curing conditions employed.

6. Concretes containing 80 kg/m^3 FA showed higher permeability compared to equal grade OPC concretes under the good and the poorest curing conditions. The permeability increases as the FA content increases, with the differences increasing with drying periods.

7. Replacing 125kg/m^3 of cement by slag results in increased oxygen permeability under 7d wet/air- and air-curing conditions.

8. Replacing 165kg/m^3 of cement by slag results also in increased oxygen permeability under 7d wet/air- and air-curing conditions, but the continuously water cured specimens showed permeability comparable to that of control and other blended cement concretes. However, the hidden inherent ability of slag/SF concretes to contribute to continued strength development through their pozzolanic/cementitious reactivity and enhanced durability and pore structure can be exploited by careful mix design and curing.

9. Oxygen permeability is related to compressive strength. This relationship is influenced by the presence of cement replacement materials and curing conditions. However, performance of concrete in a particular environment cannot be predicted

successfully from compressive strength alone, parameters such as permeability and pore structure are also required to predict the performance of concrete.

10. A correlation was found between the permeability of different blended cement concretes and the threshold diameter, as the threshold diameter increases the permeability increases. The two correlated parameters can be reduced by adequate water-curing.

CHAPTER SEVEN

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH

7.1 Overall Conclusions

Combinations of FA/SF or slag/SF used as partial replacement of cement at different levels produced concrete with high strength and acceptable microstructure. Curing conditions adopted in this research produced significant changes in the properties of concretes especially those containing high replacement levels.

Although the detailed conclusions derived from each chapter are given at the end of that chapter, the overall major conclusions regarding their mechanical properties, pore structure and permeability with and without cement replacement materials can be extracted from the test results presented in this thesis and may be summarised as follows. However these conclusions are offered within the limitation of the tests conditions and procedures, as well as the limited duration of the study period.

1. The water demand in all FA/SF and slag/SF concrete mixes was slightly higher than the control mix because of their fine particles and high surface area. This was lowered by the addition of a superplastisizer.

2. Continuous strength and microstructure development of FA/SF and slag/SF is very much inter-related to curing, therefore, it is absolutely essential to make curing an integral aspect of concrete mix design and material specifications.

3. The lower early-age strength OPC concrete incorporating either FA or slag can be compensated by the use of SF. The gain in strength is, in general, directly proportional to the percentage of the SF used.

4. At 7 days and beyond, with minor exceptions, the loss in compressive strength due to the incorporation of FA and slag can be compensated for by a given addition of SF, regardless of curing conditions. This is also true for the flexural strength.

5. The 28 day compressive and flexural strengths of FA/SF and slag/SF concrete specimens were higher than control concrete specimens under all curing

conditions with exception of 125 and 165 kg/m^3 slag mixes, exposed to air-curing.

6. The continuing increase in strength at 28, 90 and 260 days of the concrete incorporating both FA and SF or slag and SF indicates the presence of sufficient lime (liberated during the hydration of portland cement) at these ages for the pozzolanic reaction to continue.

7. Flexural strength and dynamic modulus of different concrete mixes as influenced by curing conditions were found to be reasonably well correlated with compressive strength.

8. Non-destructive test techniques such as dynamic modulus of elasticity and pulse velocity can indicate the changing of properties of FA/SF and slag/SF concrete as affected by different curing regimes. Also by these techniques the beginning of internal microcracking in concrete due to prolonged drying can be detected; this microcracking is not readily recognized by compressive strength values, and therefore, except for the case of continued wet curing, compressive strength should not be used as a criterion of concrete quality after 28 days.

9. The highest values of dynamic modulus and pulse velocity for all concrete mixes are obtained under wet curing followed by 7d wet/air and air curing conditions, respectively. The effect of drying in air and 7d wet/air curing is significantly harmful to the dynamic modulus and pulse velocity of FA/SF and slag/SF blended cement concretes, but less harmful in the plain concrete (control).

10. The performance of 165kg/m^3 slag/SF concrete on dynamic modulus and pulse velocity is better than the control, FA/SF and other slag/SF concretes under wet curing, however the differences are small. Also, the dynamic modulus and pulse velocity are more sensitive to the incorporation of FA than slag, and with relatively higher replacement levels of FA greater reductions in these properties could result.

11. In air and 7d wet/air curing conditions, the data indicate only marginal changes in total shrinkage of all concrete mixes. Also the increase in drying shrinkage resulting from the incorporation of cement replacement materials is generally marginal and might be of little practical consequence; however, the shrinkage of FA/SF concretes are slightly higher than slag/SF replacement concretes. On the

other hand, the high swelling strains of 165kg/m^3 slag/SF concrete during the period 7 to 28 days indicated the need for much longer wet curing for concrete with high slag replacement levels as well as the inadequacy of 7d wet curing.

12. The continuous wet curing of concrete is essential to achieve the highest strength, lowest total porosity and fine pore structure. Large differences in porosity and intruded pore volume values between specimens cured continuously in water and those cured in air and 7d wet/air were observed. Obviously the progress in pore structure depended on the curing regime and type and replacement level of mineral admixtures.

13. The concretes which received no curing after demoulding show the poorest performance in terms of the strength development, porosity and pore size distribution. The adverse effect of prolonged drying was equally evident in FA/SF and slag/SF blended concretes.

14. Air-cured specimens yield higher porosity values and coarser pore structure compared with continuously wet-cured specimens. The intruded pore volume for FA/SF air-cured specimens was about 40% larger than that of the wet-cured specimens, while the intruded pore volume of slag/SF concretes was 90 to 130% larger under air-curing relative to continuous wet-curing.

15. Subjecting the concretes to 7 days of wet curing, improved the pore structure of control, FA/SF and slag/SF blended mix, and significantly reduced the porosity and large pore volume of these mix as compared with the corresponding porosity and large pore volume values obtained under air-curing. Under this curing condition, the slag/SF concretes showed better performance than the FA/SF concretes i.e. lower porosity and total pore volume.

16. The pore size distribution of all concrete specimens shifts towards smaller pores as a result of continuous wet curing (progress of the pozzolanic reaction).

17. The threshold diameter is found to be very sensitive to curing, significant reductions were produced by wet curing in which slag/SF concrete specimens obtained the lowest values whereas they exhibited the highest values in air-curing.

18. The results obtained on intruded pore volume and pore structure indicate a poor performance of FA/SF concrete mixes used in this investigation. Replacing 30

and 80 kg/m^3 of cement by FA, at constant w/b ratio, results in an increase in the porosity and pore volume for the curing regimes employed in this investigation; the intruded pore volume increases with the increase in replacement of cement with FA. The pore structure also becomes coarser due to the increase in FA replacement level and drying.

19. The performance of slag/SF concrete on intruded pore volume and pore structure was better than the control and FA/SF concretes in the wet and 7d wet/air curing regimes. Replacing 80 and 165kg/m^3 of cement by slag significantly reduced the porosity and pore volume and also caused pore refinement. On the other hand replacing 125kg/m^3 of cement by slag results yielded about the same porosity and pore volume as that of 30kg/m^3 FA mix, and slightly higher porosity and pore volume than that of 165kg/m^3 slag mix.

20. The compressive strength is found to be inversely related to the total porosity. This relationship is influenced by the presence of cement replacement materials in concrete and the type of curing.

21. A good relationship was found between the large pores > 0.1 μm and the compressive strength which reveals that prolonged drying results in a coarser pore structure and lower strength, while finer pore structure and higher strength will be obtained for more wet cured concrete.

22. Oxygen permeability of concrete specimens is found to be significantly influenced by the curing conditions adopted, cement replacement materials used and age as indicated by experimental data.

23. The use of Leeds permeability cell produced satisfactory results; it is an easy and rapid test. It can be used to examine the changes in permeability as a result of changes in the curing condition and the use of cement replacement materials in concrete specimens.

24. Oxygen permeability of all concrete mixes in air and 7d wet/air curing increases as the drying time and cement replacement levels increase, and is more pronounced at air curing.

25. The continuously wet cured specimens yielded the lowest oxygen permeabilities at all curing ages compared with 7d wet/air- and air-cured specimens, these

permeability values were also lower than those reported by other researchers. However, the concretes wet-cured for 7 days show a significant improvement in permeability compared with the corresponding concretes without any curing.

26. The 30kg/m^3 FA and 80kg/m^3 slag replaced concrete showed lower permeability compared to equal grade OPC concrete under the curing conditions employed in this investigation. The 80kg/m^3 FA replaced concrete showed the opposite.

27. The 165kg/m^3 slag replaced concrete which received continuous wet-curing showed comparable permeability to that of the control and other blended cement mixes. However, 80kg/m^3 FA and 125 and 165kg/m^3 slag blended concretes were very sensitive to prolonged drying, their permeability was much more influenced by lack of early moist curing than that of other concrete mixes. This shows the importance of 7 days initial water curing for high levels of cement replacement materials concrete.

28. Oxygen permeability is related to compressive strength. This relationship is influenced by the presence of cement replacement materials and curing conditions. However, performance of concrete in a particular environment cannot be predicted successfully from compressive strength alone, parameters such as permeability and pore structure were also required to predict the performance of concrete.

29. A correlation was found between the permeability of different blended cement concretes and the threshold diameter, as the threshold diameter increases the permeability increases. The two correlated parameters can be reduced by adequate water curing.

30. Wet curing is found to be the most effective curing within the programme of this study, in providing the moisture and allowing more hydration to take place and results in better mechanical properties, finer pore structure and lower permeability. On the other hand, the results indicated that continued exposure to a drying environment of adequately cured FA/SF or slag/SF concrete can adversely affect its long-term durability. They also show that the performance of 165kg/m^3 slag/SF concrete on the properties investigated was better than the other concrete mixes.

7.2 Recommendations for Future Research

This research was carried out to obtain a high performance durable concrete with a practical range of combinations of cement replacement materials. The study of mechanical and microstructural properties under different curing regimes has identified several areas where further research is needed. The following recommendations for further research are suggested:

1. Continuing this study, other durability related properties such as chloride-generated corrosion of the embedded steel, sulphate attack, rate of carbonation should be investigated.

2. Throughout this investigation specimens were cured in the laboratory environment at 20°C. It is of interest to study the performance of these FA/SF and slag/SF blended mixes under aggressive environments such as sea water and hot/dry regimes.

3. Satisfactory oxygen permeability values are obtained in this investigation; however, a further study on permeability of FA/SF and slag/SF concretes to water as well as chloride under practical curing conditions requires an in-depth examination to accumulate enough data in order to give a clear understanding of the degree of influence in the permeabilities of concrete brought by the combination of these cement replacement materials.

4. In this investigation mercury intrusion porosimetry tests were performed at 260 days (a more desirable age especially when supplementary cementing materials are being used), however, for comparison purposes the size distribution and total porosity of FA/SF and slag/SF concretes under different curing conditions is required to be studied at early ages (7 and 28 days). It is also required to conduct a study into the effect of drying regimes on the pore size distribution as measured by mercury porosimetry and oxygen permeability as measured by gas permeameter.

5. The pore structure and oxygen permeability in this study are conducted on concrete specimens cast especially for this purpose. It would have been preferable and more practical for the researchers in this field to execute experiments on concrete samples rather than cement or mortar specimens cast, and the results are more likely to be representative of that in concrete.

6. The mechanical properties, pore structure and permeability of concrete with a combination of 10% SF and either 40% FA or 40 to 60% slag by weight of cement are considerably different to those of normal Portland cement concrete; thus it is recommended to be investigated, and long-term tests are to be carried out to settle its durability issue.

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